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2,3-Difluorinated phenyl and cyclohexane units in the design and synthesis of liquid crystals having negative dielectric anisotropy

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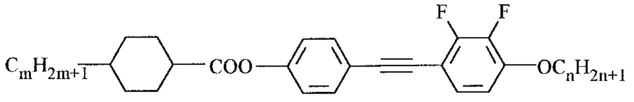
Three homologous series of new compounds containing 2,3-difluorophenylene and *trans*-1,4-substituted cyclohexane have been synthesized by a coupling reaction with $Pd(PPh_3)_2Cl_2$ as the catalyst. Their liquid crystalline properties have been studied by optical polarizing microscopy and DSC. The relationship between the properties and chemical structures of the target compounds is discussed in detail.

1. Introduction

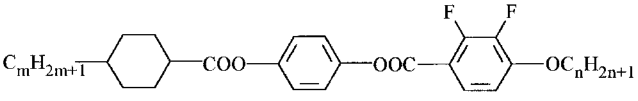
With the development of multimedia liquid crystal displays (LCDs), a strong demand has been created for new liquid crystalline materials with high clearing temperatures, high dielectric anisotropy ($\Delta\varepsilon$), and low viscosity. Liquid crystals with fluorinated aromatic substructures meet most of these criteria and are now commonly used as major components of LC mixtures with fast response times [1].

Currently, most active matrix displays use liquid crystal mixtures with a positive dielectric anisotropy. In contrast, the recently introduced VA-TFT LCD (vertical alignment thin film transistor LCD) [2]—which offers a superior picture quality with a wide viewing angle (160°), high contrast, and video-compatible switching times (< 20 ms)—is based on a liquid crystal mixture with negative dielectric anisotropy. In earlier technically applicable materials [3], the negative $\Delta\varepsilon$ was achieved by means of the strong perpendicular dipole moment of a cyano group. However, nitriles in general have relatively high viscosity, which leads to longer switching times. Nowadays, the materials with negative $\Delta\varepsilon$ are mostly based on laterally fluorinated phenyl groups [2].

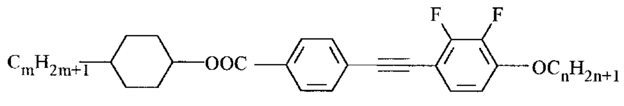
In previous studies, we synthesized and reported many types of useful liquid crystal materials containing symmetrical tetrafluoro-substitution of phenyl groups, and obtained several rules concerning fluorinated LCs [4–7]. But, because of the symmetrical fluorine substitution, the dielectric anisotropy perpendicular to the molecular axis is low. In the search for new materials with high $\Delta\varepsilon$, we introduced 2,3-difluorinated phenyl into the molecules. Due to the strong dipole moment of the C–F bond, arenes with 2,3-difluorine substituents may be well suited for achieving a strongly negative dielectric anisotropy. Unfortunately, the strongly negative $\Delta\varepsilon$ was obtained at the expense of decrease of the clearing temperatures by about 25–30 K per fluorine substituent [1]. To compensate for the disadvantages caused by fluorinated phenyl groups, we have introduced *trans*-1,4-substituted cyclohexane (which usually increases the clearing temperature as well as decreasing birefringence) into the LC molecules and synthesized three novel types of compounds (**A**, **B** and **C**).



A: m = 2, 3, 4, 5; n = 3, 4, 5, 6, 7, 8, 9, 10, 12



B: m = 5; n = 3, 4, 5



C: m = 5; n = 9

2. Synthesis

The target compounds were prepared according to the scheme.

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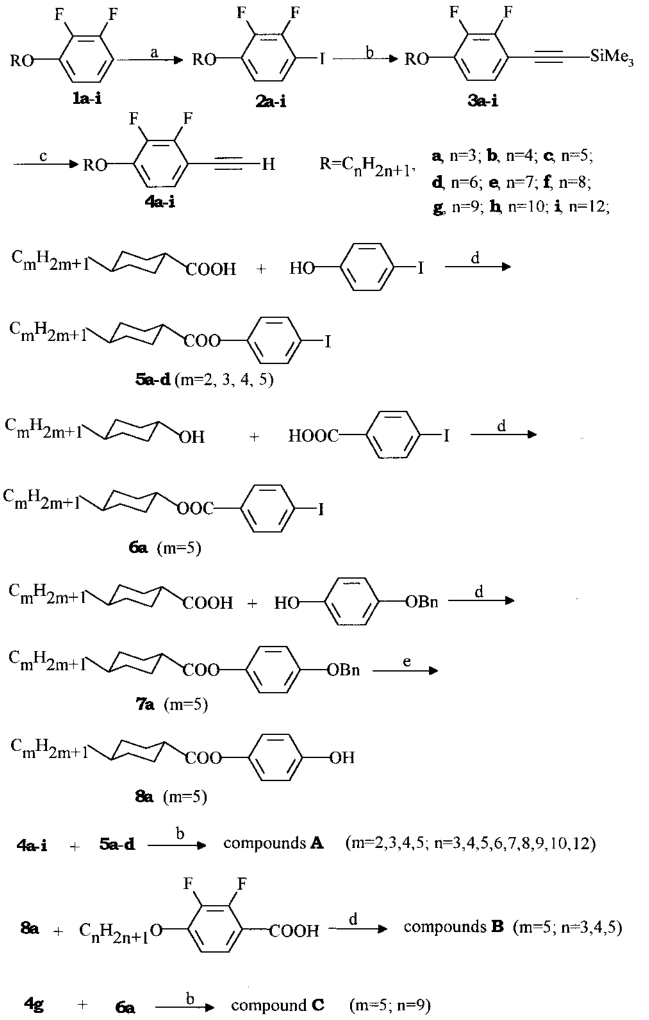

Scheme. conditions and reagents: a (1) BuLi/THF, − 78°C (2) I_2/THF, − 78°C—r.t. b trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N. c NaOH, methanol/acetone, r.t. d DCC, DMAP, THF, r.t. e H_2, Pd/C, alcohol, 60°C.

The compounds **1a–i**, **5a–d**, **6a**, **7a**, **8a** and **B** were prepared by reported methods [4, 8]. Compounds **2a–i** were synthesized from compounds **1a–i** by BuLi/THF and I_2/THF at − 78°C. The coupling reaction between compounds **2a–i** and trimethylsilylacetylene using the catalysts $Pd(PPh_3)_2Cl_2$ and CuI in dry Et_3N gave compounds **3a–i**, from which **4a–i** were obtained after the removal of the trimethysilyl group under the action of methanol and aqueous NaOH in acetone. The target compounds **A** and **C** could be obtained by coupling reaction of compounds **4a–i** with **5a–d** and **6a** using $Pd(PPh_3)_2Cl_2$ as catalyst.

All of the final compounds were purified by chromatography on silica gel with petroleum ether (b.p. 60–90°C)/ethyl acetate (20:1) as eluent, and were recrystallized from acetone/methanol. Their structures were characterized by elemental analysis, IR, MS, ^{1}H NMR and ^{19}F NMR. Phase transitions were studied by thermal polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). For the microscopic observations we used a Mettler FP-80 hot stage and FP-82 control unit in conjunction with an Olympus PM-6 polarizing microscope; the results were confirmed using a DSC Shimadzu-50 calorimeter with data system; heating and cooling rates were 5°C min^{-1}.

3. Experimental

IR spectra were recorded on a BioRad FTS-185 spectrometer. ^{1}H NMR spectra with TMS as internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM 360L spectrometer (60 MHz) or an FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra, the high field is positive. Mass spectra were measured on a Finnigan-4021 spectrometer.

3.1. *4-n-Heptyloxy-2,3-difluoro-1-iodobenzene, 2e*

Butyl-lithium (1.6M in hexane, 3.5 ml, 5.6 mmol) was added dropwise to a stirred, cooled (− 78°C) solution of compound **1e** (1.004 g, 4.4 mmol) in dry THF (30 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 1.5 h and then a previously cooled solution of I_2 (1.34 g, 5.47 mmol) in dry THF (20 ml) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight and then a saturated solution of NH_4Cl was added. The product was extracted into ether (twice), and the combined etheral extracts were washed with a saturated solution of $Na_2S_2O_3$ and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether as eluent to give a colourless liquid (1.162 g, 76.4%). ^{1}H NMR ($CDCl_3$/TMS): 0.89 (t, 3H, $J = 6.89$ Hz); 1.25–1.85 (m, 10H); 4.01 (t, 2H, $J = 6.57$ Hz); 6.57 (M, 1H, Harom); 7.36 (m, 1H, Harom). ^{19}F NMR ($CDCl_3$/TFA: 39.0 (m, 1F); 77.0 (m, 1F). MS (*m*/*z*, %): 354 (M^+, 5.06).

3.2. *4-n-Heptyloxy-2,3-difluorophenyl trimethylsilylacetylene, 3e*

In a dry 100 ml round-bottom three-necked flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser attached to a bubble, were placed 3.54 g (10 mmol) of compound **2e**, 980 mg (10 mmol) of trimethylsilylacetylene, 30 mg (0.043 mmol) of $Pd(PPh_3)_2Cl_2$ and 17 mg (0.089 mmol) of copper(I) iodide. Anhydrous triethylamine (50 ml) was added to the reaction mixture under nitrogen. The resulting mixture was heated at 60°C in an oil-bath while stirring for 3 h, during which time a brown precipitate formed. Analysis by TLC revealed a completed reaction. The precipitate was removed by filtration, and washed with ether. The filtrate was washed with ether and water, and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as eluent to yield a colourless liquid (2.27 g, 70.0%). ^1H NMR ($CDCl_3$/TMS): 0.20 (s, 9H, $3 \times CH_3$), 0.89 (t, 3H, $J = 6.00$ Hz), 1.25–2.00 (m, 10H), 4.00 (t, 2H, $J = 6.00$ Hz), 6.65 (M, 1H, Harom); 7.20 (m, 1H, Harom). ^{19}F NMR ($CDCl_3$/TFA): 57.0 (m, 1F); 82.0 (m, 1F).

3.3. *4-n-Heptyloxy-2,3-difluorophenylacetylene,* ***4e***

In a 50 ml round-bottom flask equipped with a magnetic stirring bar, were placed 1.62 g (5 mmol) of compound **3e**, 6 ml of methanol, 25 ml of acetone and 3 ml of 0.2N aqueous NaOH. The reaction mixture was stirred at room temperature for 24 h. The organic solvent was then removed *in vacuo*, and the product extracted with ether. The etheral extracts were washed with water, and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as eluent to give a colourless liquid (1.134 g, 90.0%). ^1H NMR ($CDCl_3$/TMS): 0.89 (t, 3H, $J = 6.62$ Hz); 1.26–1.93 (m, 10H); 3.24 (s, 1H); 4.03 (t, 2H, $J = 6.55$ Hz); 6.67 (M, 1H, Harom); 7.15 (m, 1H, Harom). ^{19}F NMR ($CDCl_3$/TFA): 57.5 (m, 1F); 82.0 (m, 1F). MS (*m*/*z*, %): 252 (M^+, 5.06).

3.4. *4-(4-n-Heptyloxy-2,3-difluorophenyl)acetylenylphenyl trans-4-pentyl cyclohexyl-1-carboxylate,* $\mathbf{A_{5\text{-}8}}$

Under dry nitrogen, to a mixture of 4-*n*-octyloxy-2,3-difluorophenylacetylene (106.4 mg, 0.4 mmol), 4-iodophenyl *trans*-4-*n*-pentylcyclohexyl-1-carboxylate (160 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 0.0043 mmol) and copper(I) iodide (17 mg, 0.089 mmol), was added anhydrous triethylamine (15 ml). The resulting mixture was heated under reflux with stirring for 4 h. Analysis by TLC revealed that the reaction was complete. The precipitate was removed by filtration and washed with ether. The filtrate was washed with water and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ ethyl acetate (20:1) as eluent to give yellow crystals; these were recrystallized from acetone/methanol to yield white crystals (161 mg, 74.8%), m.p. 50.3°C. ^1H NMR ($CDCl_3$/TMS): 0.70–2.70 (m, 36H), 4.10 (t, 2H, $J = 6.00$ Hz), 6.70 (m, 1H, Harom), 7.10 (m, 1H), 7.05 (d, 2H)/7.55 (d, 2H) ($J = 9.00$ Hz, Harom). ^{19}F NMR ($CDCl_3$/TFA): 56.5 (m, 1F), 80.5 (m, 1F). IR (KBr, cm^{-1}): 2922 2854 2214 1753 1515 1397 1163 1081 981 798 725 532. MS (*m*/*z*, %): 538 (M^+, 17.64). Anal. Calcd for $C_{34}H_{44}F_2O_3$: C 75.80, H 8.23, F 7.05; found: C 75.80, H 8.35, F 7.19%.

The other compounds in the A and C series have been prepared following the same general procedure. All of the new target compounds had satisfactory elemental analysis and appropriate ^1H and ^{19}F NMR, IR and MS spectral data.

All of the intermediates had satisfactory ^1H and ^{19}F NMR spectral data.

4. Results and discussion

Phase transition temperatures for the target compounds are listed in the table. Figure 1 shows a plot of the transition temperatures as a function of alkoxy chain length (*n*) of series **A** (when $m = 5$). Compounds with short alkoxy chain length exhibit only the nematic phase. As the chain length increases, the tendency to form the smectic phase increases at the expense of the nematic phase. This is due to the larger lateral intermolecular attractive force and the smaller terminal intermolecular cohesions. The melting points of series **A** (when $m = 5$) change regularly. When $n \leq 6$, higher melting points for odd carbon numbers are observed, whereas when $n \geq 7$, lower ones are observed. Clearing points decrease with increasing alkoxy chain length.

As far as the influence of the alkyl chain length is concerned (see figure 2), with increasing *m*, the melting and clearing points have a slight increasing trend; but the thermal stability of the smectic A phase changes greatly. With increasing length of alkyl chain, the nematic phase range decreases and the smectic range increases.

In order to study the effect of the centre linking group of ester bond and acetylenic bond on the phase transition, we plot in figure 3 the transition temperatures of series **A** and **B** (when $m = 5$) against the number of carbon atoms in alkoxy chain, *n*. It can be clearly seen that the clearing points of series **A** are higher than those

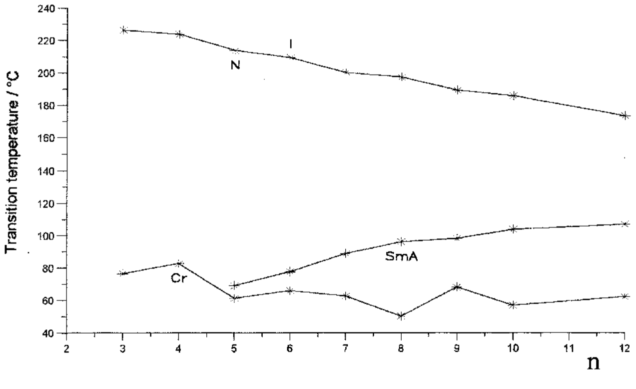

Figure 1. Transition temperature versus *n* for series **A** ($m = 5$).

Table. Phase transition temperatures (°C) of target compounds. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic, Rec = recrystal.

Compounds	*m*	*n*	Transition temperatures/°C
$\mathbf{A}_{2\text{-}8}$	2	8	Cr 55.6 N 178.8 I 178.4 N 30.8 Rec
$\mathbf{A}_{3\text{-}8}$	3	8	Cr 43.8 SmA 50.3 N 198.7 I 198.0 N 49.5 SmA 27.4 Rec
$\mathbf{A}_{4\text{-}8}$	4	8	Cr 57.4 SmA 77.7 N 195.9 I 195.2 N 76.8 SmA 25.1 Rec
$\mathbf{A}_{5\text{-}3}$	5	3	Cr 76.6 N 226.3 I 225.4 N 65.2 Rec
$\mathbf{A}_{5\text{-}4}$	5	4	Cr 82.8 N 223.8 I 223.1 N 54.9 Rec
$\mathbf{A}_{5\text{-}5}$	5	5	Cr 61.3 SmA 69.1 N 213.7 I 213.0 N 68.7 SmA 46.7 Rec
$\mathbf{A}_{5\text{-}6}$	5	6	Cr 86.1 SmA 77.8 N 209.3 I 208.6 N 77.4 SmA 35.9 Rec
$\mathbf{A}_{5\text{-}7}$	5	7	Cr 62.8 SmA 88.9 N 200.2 I 199.7 N 88.2 SmA 31.5 Rec
$\mathbf{A}_{5\text{-}8}$	5	8	Cr 50.3 SmA 96.1 N 197.2 I 196.9 N 95.3 SmA 28.8 Rec
$\mathbf{A}_{5\text{-}9}$	5	9	Cr 68.3 SmA 98.1 N 189.1 I 188.4 N 97.3 SmA 54.1 Rec
$\mathbf{A}_{5\text{-}10}$	5	10	Cr 56.9 SmA 103.7 N 185.6 I 184.8 N 103.1 SmA 31.7 Rec
$\mathbf{A}_{5\text{-}12}$	5	12	Cr 62.2 SmA 106.8 N 173.1 I 172.2 N 105.3 SmA 42.6 Rec
$\mathbf{B}_{5\text{-}3}$	5	3	Cr 115.5 N 219.6 I 219.1 N 92.4 Rec
$\mathbf{B}_{5\text{-}4}$	5	4	Cr 116.3 N 215.7 I 215.1 N 98.6 Rec
$\mathbf{B}_{5\text{-}5}$	5	5	Cr 91.7 SmA 95.1 N 206.0 I 205.8 N 94.1 SmA 61.8 Rec
$\mathbf{C}_{5\text{-}9}$	5	9	Cr 81.1 N 161.3 I 160.8 N 39.6 Rec

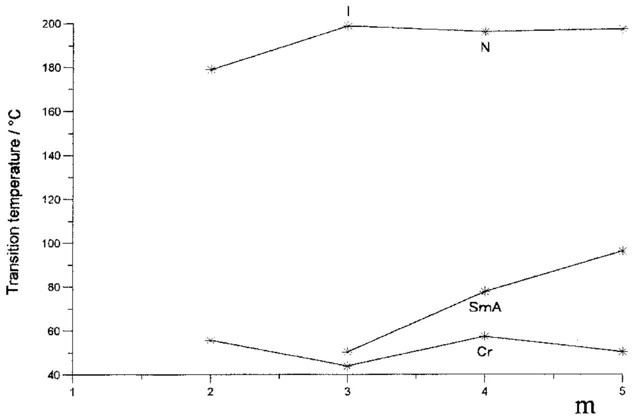

Figure 2. Transition temperature versus *m* for series $\mathbf{A}_{m\text{-}8}$ ($m = 8$).

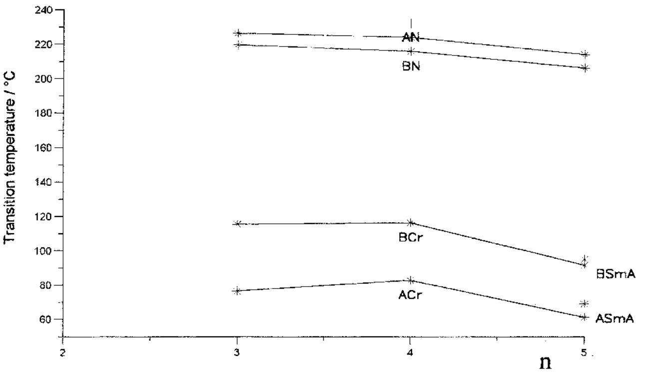

Figure 3. Transition temperature versus *n* for series **A** and **B** ($m = 5$).

of series **B**; this is consistent with the extent of conjugation in the molecules. The region of conjugation in series **A** compounds, which have an acetylenic bond as a linking group between two benzene rings, is much larger than that in series **B** compounds, which have an ester linking group. Moreover, molecules containing the ester bond have stronger lateral intermolecular cohesions, which favour a tight packing of the molecules. Thus the melting points and thermal stability of the smectic phase for series **B** are much higher than those of series **A**.

From the comparison between the transition temperatures of compounds $\mathbf{A}_{5\text{-}9}$ and $\mathbf{C}_{5\text{-}9}$, we note that $\mathbf{C}_{5\text{-}9}$ has higher melting and lower clearing points than the equivalent **A** series homologue with the same terminal alkoxy and alkyl chains. Furthermore, compound $\mathbf{A}_{5\text{-}9}$ exhibits both smectic A and nematic phases whereas $\mathbf{C}_{5\text{-}9}$ shows only the nematic phase. It appears that the direction of the linking ester bond significantly changes the liquid crystal phase and transition temperatures. This may be the result of the decreasing anisotropy of molecular shape when changing the direction of the ester bond from the **A** compound to the **C** compound.

In conclusion, for series **A**, the alkoxy chain length (*n*) has a great effect on the thermal stabilities of both smectic and nematic phases, while the alkyl chain length (*m*) affects the smectic phase greatly. A comparison of series **A** and series **B** compounds shows that the acetylenic linking bond, rather than the ester bond, is preferable for mesophases. The direction of the ester bond has a significant effect on the mesogenic behaviour, which can be seen clearly from the comparison of compounds $\mathbf{A}_{5\text{-}9}$ and $\mathbf{C}_{5\text{-}9}$.

The compounds in series **A** and **B** may have large negative anisotropy ($-\Delta\varepsilon$) because of the 2,3-difluorobenzene subunit. Further studies on the measurement of the $\Delta\varepsilon$ of these compounds are currently in progress and will be reported in a future paper.

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