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## Liquid Crystals

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### Novel fluorinated liquid crystals. II. The synthesis and phase transitions of a novel type of ferroelectric liquid crystals containing 1,4-tetrafluorophenylene moiety

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## Novel fluorinated liquid crystals

### II. The synthesis and phase transitions of a novel type of ferroelectric liquid crystals containing 1,4-tetrafluorophenylene moiety

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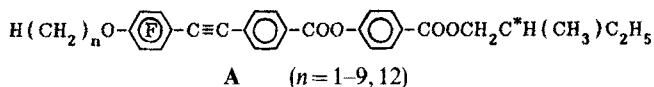
(Received 19 January 1993; accepted 26 July 1993)

4-[(S)-2-Methylbutoxycarbonyl]phenyl 4-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoates have been prepared from the starting material 1-pentafluorophenyl-2-trimethylsilylacetylene. Polarizing microscope textural observation and DSC measurements of the phase transitions of these novel compounds showed that they were liquid crystals with chiral smectic C phase ( $S_C^*$ ), smectic A ( $S_A$ ) and cholesteric (Ch) phases. The effects of the alkoxy chain length on the transition temperatures and enthalpies were also studied.

#### 1. Introduction

In 1975 Meyer *et al.* [1], showed that the chiral smectic C phase ( $S_C^*$ ) was ferroelectric. The technological importance of this discovery was realized when Clark and Lagerwall [2] made the first electro-optical device based in the  $S_C^*$  phase. Since then there has been much more interest in ferroelectric liquid crystals and displays based on the ferroelectric chiral smectic C phase. These ferroelectric displays can offer both very fast response time ( $\mu$ s rather than ms) and high multiplexability due to the inherent bistability, so they have great potential as fast switching devices which have wide applications in message-transportation and image-displaying.

In recent years, much research attention has been paid to liquid crystals containing fluorine atoms in backbone structures or end chains, in order to find out new liquid crystals with better physical properties; hundreds of liquid crystalline materials with monofluoro- or difluoro-substituted aromatic rings have been prepared [3-7]. Nevertheless, only a limited number of liquid crystal materials with 1,4-disubstituted tetrafluorobenzene rings have been reported. These compounds are mainly Schiff's bases [8, 9], biphenylene diamines [10], terephthalates with one, two or three perfluorinated 1,4-phenylene groups [11], perfluorinated hydroquinone bisbenzoates [12], 4-*n*-alkoxyperfluorobenzoates [13-16], and 4-alkoxycarbonylperfluorophenyl esters [17-20]. We therefore aimed to synthesize new liquid crystal compounds with 2,3,5,6-tetrafluoro-1,4-phenylene in the skeleton structures so as to search out new materials for display devices and other applications [21]. In this paper, we have now prepared a novel type of ferroelectric liquid crystal material (the compounds A) using 1-pentafluorophenyl-2-trimethylsilylacetylene as the starting material.

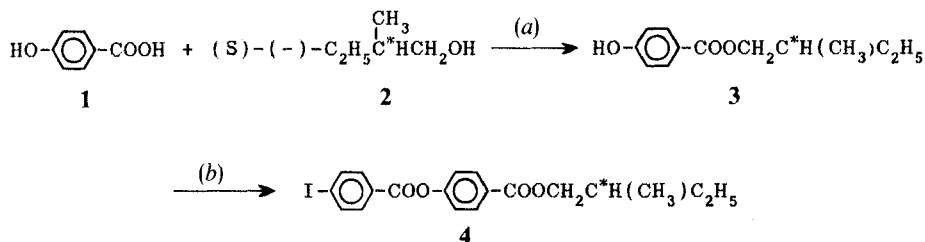


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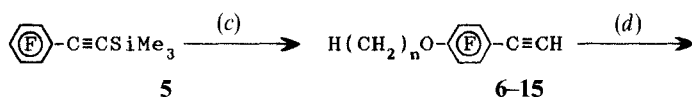
The compounds reported here are the subject of a patent application [22] which also covers a wide range of other related systems.

## 2. Synthesis

The preparation of the required mesogens was based on a palladium catalysed coupling reaction involving polyfluorophenylacetylene and an appropriate aryl iodide (see scheme 2). In the first step, (*S*)-2-methylbutyl 4-hydroxybenzoate (compound **3**, see scheme 1) was prepared from an esterification reaction between 4-hydroxybenzoic acid and (*S*)-2-methyl-1-butanol with thionyl chloride as acylating promoter, carried out at low temperature (0–70°C). In this step, the configuration of the chiral carbon atom was preserved. The mild one pot esterification [23] between compound **3** and 4-iodobenzoic acid in the presence of both dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine (PPY) catalyst in anhydrous ether gave the desired compound **4**. In our previous study, we reported the synthesis of 1-pentafluorophenyl-2-trimethylsilylacetylene [24]. Therefore the 4-*n*-alkoxy-2,3,5,6-tetrafluorophenylacetylenes (compounds **6–15**) were easily obtained from compound **5** by



Scheme 1. (a)  $\text{SOCl}_2$ , 0–70°C, (b) 4-I-C<sub>6</sub>H<sub>4</sub>-COOH, DCC, PPY, Et<sub>2</sub>O, R.T.

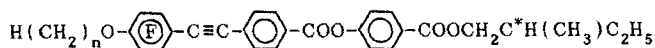


**6**,  $n=1$ ; **7**,  $n=2$ ; **8**,  $n=3$ ;

**9**,  $n=4$ ; **10**,  $n=5$ ; **11**,  $n=6$ ;

**12**,  $n=7$ ; **13**,  $n=8$ ; **14**,  $n=9$ ;

**15**,  $n=12$ .



**16–25**

**16**,  $n=1$ ; **17**,  $n=2$ ; **18**,  $n=3$ ; **19**,  $n=4$ ; **20**,  $n=5$ ;

**21**,  $n=6$ ; **22**,  $n=7$ ; **23**,  $n=8$ ; **24**,  $n=9$ ; **25**,  $n=12$ .

Scheme 2. (c)  $\text{K}_2\text{CO}_3$ , DMF,  $\text{H}(\text{CH}_2)_n\text{OH}$ , R.T., (d) compound **4**, CuI, Et<sub>3</sub>N,  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ , reflux.

nucleophilic substitution with a *n*-alkanol at room temperature using  $K_2CO_3$  as base [25,26] (scheme 2). Finally the coupling reaction between compounds **4** and **6–15** under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in anhydrous triethylamine gave the desired polyfluoro-substituted system (compounds **16–25**).

All of the final compounds prepared are mesomorphic. Phase transitions were studied using a Mettler FP 52 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope and a Perkin–Elmer DSC 7 instrument, while phase identification was made by comparing the observed textures with those in the literature [27,28].

### 3. Results and discussion

The liquid crystal transition temperatures and enthalpies of transition for these new materials are presented in tables 1 and 2.

#### 3.1. Optical microscopy studies

Most of the new compounds exhibit enantiotropic Ch,  $S_A$  and  $S_C^*$  phases. However, the compound for  $n = 1$  does not display an  $S_A$  phase, and the compounds for  $n = 2$  and  $n = 3$  exhibit monotropic  $S_C^*$  and enantiotropic  $S_A$  and Ch phases. It is interesting to

Table 1. Phase transition temperatures ( $^{\circ}C$ ) of the compounds A.

<i>n</i>	Phase transition temperatures/ $^{\circ}C$ †					
1	C	$\xrightarrow{100.8}$	Ch	$\xleftrightarrow{162.4}$	I	
		$\xleftarrow{72.7} S_C^*$	$\xleftarrow{100.5}$	$\xleftarrow{162.0}$		
2	C	$\xrightarrow{95.4}$	$S_A$	$\xleftrightarrow{110.3}$	I	$\xleftrightarrow{174.7}$ I
		$\xleftarrow{58.8} S_C^*$	$\xleftarrow{95.1}$	$\xleftarrow{109.6}$		$\xleftarrow{174.2}$
3	C	$\xrightarrow{93.6}$	$S_A$	$\xleftrightarrow{118.0}$	Ch	$\xleftrightarrow{164.4}$ I
		$\xleftarrow{62.2} S_C^*$	$\xleftarrow{93.4}$	$\xleftarrow{117.2}$		$\xleftarrow{164.1}$
4	C	$\xleftrightarrow{90.4}$	$S_C^*$	$\xleftrightarrow{90.8}$	$S_A$	$\xleftrightarrow{136.0}$ Ch $\xleftrightarrow{169.2}$ I
		$\xleftarrow{73.7}$	$\xleftarrow{90.6}$	$\xleftarrow{135.7}$		$\xleftarrow{168.8}$
5	C	$\xleftrightarrow{89.5}$	$S_C^*$	$\xleftrightarrow{90.0}$	$S_A$	$\xleftrightarrow{124.7}$ Ch $\xleftrightarrow{153.1}$ I
		$\xleftarrow{70.6}$	$\xleftarrow{89.7}$	$\xleftarrow{124.2}$		$\xleftarrow{152.9}$
6	C	$\xleftrightarrow{88.8}$	$S_C^*$	$\xleftrightarrow{89.8}$	$S_A$	$\xleftrightarrow{132.8}$ Ch $\xleftrightarrow{154.7}$ I
		$\xleftarrow{70.3}$	$\xleftarrow{89.5}$	$\xleftarrow{132.4}$		$\xleftarrow{154.5}$
7	C	$\xleftrightarrow{77.8}$	$S_C^*$	$\xleftrightarrow{78.6}$	$S_A$	$\xleftrightarrow{129.6}$ Ch $\xleftrightarrow{147.5}$ I
		$\xleftarrow{61.6}$	$\xleftarrow{78.0}$	$\xleftarrow{129.0}$		$\xleftarrow{147.2}$
8	C	$\xleftrightarrow{75.4}$	$S_C^*$	$\xleftrightarrow{77.7}$	$S_A$	$\xleftrightarrow{129.4}$ Ch $\xleftrightarrow{144.8}$ I
		$\xleftarrow{58.8}$	$\xleftarrow{77.2}$	$\xleftarrow{129.1}$		$\xleftarrow{144.4}$
9	C	$\xleftrightarrow{74.0}$	$S_C^*$	$\xleftrightarrow{80.0}$	$S_A$	$\xleftrightarrow{128.3}$ Ch $\xleftrightarrow{139.3}$ I
		$\xleftarrow{53.3}$	$\xleftarrow{79.6}$	$\xleftarrow{128.0}$		$\xleftarrow{139.2}$
12	C	$\xleftrightarrow{72.9}$	$S_C^*$	$\xleftrightarrow{81.6}$	$S_A$	$\xleftrightarrow{127.4}$ Ch $\xleftrightarrow{132.1}$ I
		$\xleftarrow{54.4}$	$\xleftarrow{81.2}$	$\xleftarrow{127.0}$		$\xleftarrow{132.0}$

† C, crystal; S, smectic; Ch, cholesteric; I, isotropic.

Table 2. Transition enthalpies  $\Delta H$  [kJ mol<sup>-1</sup>] of the compounds A.

<i>n</i>	$\Delta H_{C \rightarrow S}$	$\Delta H_{S_A \rightarrow Ch}$	$\Delta H_{Ch \rightarrow I}$	$\Delta H_{I \rightarrow Ch}$	$\Delta H_{Ch \rightarrow S_A}$	$\Delta H_{S_C^* \rightarrow C}$
1	33.93†	–	0.30	–0.32	–	–24.51
2	30.80	0.18	0.42	–0.42	–0.16	–25.26
3	24.19	0.29	0.44	–0.38	–0.29	–21.89
4	26.61	0.60	0.45	–0.42	–0.65	–22.40
5	26.08	0.36	0.41	–0.37	–0.31	–22.85
6	24.15	0.60	0.43	–0.45	–0.61	–22.36
7	23.22	0.53	0.39	–0.37	–0.53	–23.98
8	25.49	0.70	0.45	–0.53	–0.63	–25.39
9	27.02	0.64	0.49	–0.48	–0.73	–25.37
12	34.15	1.44	0.70	–0.71	–1.31	–31.12

† The phase transition in C → Ch.

note that all of the new fluorinated materials have a wide temperature range of mesophase and a good phase sequence, so they are of potential as new ferroelectric liquid crystals which could be employed in switching and display devices. The physical properties of these novel fluorinated liquid crystals are being studied.

As far as the influence of the end chain is concerned, first of all, the melting points for this homologous series of compounds fall with lengthening alkoxy chain. Secondly, both the thermal stability of the S<sub>A</sub> phase and that of the S<sub>C</sub><sup>\*</sup> phase increase whilst that of the Ch phase decreases as the terminal alkoxy chain is lengthened. Moreover, the clearing points vary with a regular odd–even effect [29, 30] provided that the alkoxy chain is not too long (*n* < 8); the alteration of the clearing points then decreases with growth of the terminal chain.

### 3.2. Calorimetric studies

This study was performed with a Perkin–Elmer DSC 7.

The melting enthalpy varies from 23 to 35 kJ mol<sup>-1</sup> and the average value is 27.56 kJ mol<sup>-1</sup>. The S<sub>A</sub>–Ch and Ch–I transition enthalpies are found to be between 0.18 and 1.44 kJ mol<sup>-1</sup> and increase with the chain length. The S<sub>C</sub><sup>\*</sup>–S<sub>A</sub> transition enthalpy is very weak and not detected by DSC analysis.

Obviously, the heat changes of the transition from the mesophase to the isotropic liquid are much smaller than those involved at the melting points (solid–mesophase), and so are the S<sub>A</sub>–Ch transition enthalpies. However, the S<sub>A</sub>–Ch and Ch–I transition enthalpies are very close.

## 4. Experimental

IR spectra were recorded on a Shimadzu IR-440 spectrophotometer, using KBr pellets of solids or films of liquids. <sup>1</sup>H NMR spectra were obtained with TMS as internal standard and <sup>19</sup>F NMR spectra with trifluoroacetic acid (TFA) as external standard and were recorded on a Varian EM 360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For <sup>19</sup>F NMR spectra, high field is positive. Mass spectra were recorded using a Finnigan-4021 spectrometer. Specific rotation values were measured using a Perkin–Elmer 241MC Polarimeter.

Compound **5** was prepared as described in a previous publication [24].

4.1. (*S*)-2-Methylbutyl 4-hydroxybenzoate (3)

Thionyl chloride (2.0 ml, 3.3 g, 0.028 mol) was added slowly, dropwise to a stirred, cooled (0°C) mixture of 4-hydroxybenzoic acid (2.8 g, 0.02 mol) and (*s*)-(-)-2-methyl-1-butanol (5.0 g, 0.057 mol), over a period of 5 min. Then the reaction mixture was allowed to warm to room temperature, stirred at 30–35°C for 3 h and at 60°C for 21 h, until TLC analysis revealed complete reaction. The excess of alcohol was recovered by vacuum distillation and the residue was dissolved in 80 ml of ether. The solution of the crude product was washed with 10 per cent aqueous NaHCO<sub>3</sub> (3 × 50 ml), water (3 × 40 ml), and dried using anhydrous sodium sulphate. Then the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel, with petroleum ether (b.p. 60–90°C)/ethyl acetate (7 : 3) as eluent, to yield a pale yellow oil-like liquid.

Yield 2.86 g (67.2 per cent);  $[\alpha]_D^{20}$  (CHCl<sub>3</sub>): +6.01°; <sup>1</sup>H NMR(CCL<sub>4</sub>/TMS): δ 0.95–2.0(m, 9 H, CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>), 4.13(d, 2 H, *J* = 6.0 Hz, COOCH<sub>2</sub>) 6.90(d, 2 H)/7.93(d, 2 H) (AA'BB', *J* = 8.0 Hz, H<sub>arom</sub>), 8.24(s, 1 H, OH).

4.2. 4-[(*s*)-2-Methylbutoxycarbonyl]phenyl 4-iodobenzoate (4)

Quantities: 4-iodobenzoic acid (2.7 g, 10.9 mmol), compound 3 (2.3 g, 11.0 mmol), *N,N*-dicyclohexylcarbodiimide (3.0 g, 14.6 mmol), 4-pyrrolidinopyridine (150 mg, 1.0 mmol), anhydrous diethyl ether (40 ml); reaction time: 120 h. The experimental procedure was as described in [23]. Analysis by TLC indicated completion of reaction. The crude product was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (9 : 1) as eluent to yield white flaky crystals of 4.

Yield 3.48 g (72.0 per cent); m.p. 63.1°C;  $[\alpha]_D^{20}$  (CHCl<sub>3</sub>): +3.12°; <sup>1</sup>H NMR(CCL<sub>4</sub>/TMS): δ 0.90–2.0(m, 9 H, CH(CH<sub>3</sub>)C<sub>2</sub>H<sub>5</sub>), 4.07(d, 2 H, *J* = 6.0 Hz, COOCH<sub>2</sub>), 7.22(d, 2 H) 8.07(d, 2 H) (AA'BB', *J* = 8.4 Hz, COO–C<sub>6</sub>H<sub>4</sub>–COO), 7.83 (s, 4 H, I–C<sub>6</sub>H<sub>4</sub>–COO).

4.3. 4-*n*-Dodecyloxy-2,3,5,6-tetrafluorophenylacetylene (15)

A typical procedure: A mixture of compound 5 (1.0 g, 3.78 mmol), 1-dodecanol (1.90 g, 10.0 mmol), DMF (2.0 ml) and potassium carbonate (1.0 g, 7.24 mmol) was stirred at room temperature for 120 h. <sup>19</sup>F NMR analysis revealed the disappearance of compound 5. Then 20 ml of ether and 15 ml of water were added with stirring to the resulting mixture. The organic layer was separated and the aqueous layer was shaken with ether (3 × 15 ml). The combined ethereal extracts were washed with water (3 × 10 ml) and dried over anhydrous sodium sulphate. Then the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel/petroleum ether (b.p. 60–90°C)) to yield a pale yellow liquid.

Yield 1.11 g (81.8 per cent); <sup>1</sup>H NMR(CCL<sub>4</sub>/TMS): δ 0.80–1.80(m, 23 H, (CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>), 3.30(s, 1 H, C≡CH), 4.10(t, 2 H, *J* = 6.0 Hz, OCH<sub>2</sub>); <sup>19</sup>F NMR (CCL<sub>4</sub>/TFA): δ 60.50(d, 2 F, *J* = 18.8 Hz, F<sub>arom</sub>), 80.40(d, 2 F, *J* = 18.8 Hz, F<sub>arom</sub>).

Compounds 6–14 were prepared similarly, and all of them had appropriate <sup>1</sup>H and <sup>19</sup>F NMR spectral data.

4.4. 4-[(*S*)-2-Methylbutoxycarbonyl]phenyl 4-[(4-*n*-dodecyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (25)

A typical procedure: To a mixture of compound 4 (400 mg, 0.913 mmol), compound 15 (328 mg, 0.916 mmol), bis(triphenylphosphine)palladium dichloride (30 mg,

0.043 mmol) and copper(I) iodide (20 mg, 0.105 mmol), under dry nitrogen, was added 15 ml of anhydrous triethylamine. The resulting mixture was boiled with stirring for 2 h. TLC analysis denoted completion of reaction. Then the precipitate was filtered off and washed with ether and the filtrate washed with water, and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel, using petroleum ether (b.p. 60–90°C)/ethyl acetate (9:1) as eluent, to yield pale yellow crystals. Recrystallization from acetone–methanol gave white flaky crystals of **25**.

Yield 554 mg (90.8 per cent); m.p. 72.9°C;  $[\alpha]_D^{20}$  (CHCl<sub>3</sub>): +1.77°; <sup>1</sup>H NMR(CCl<sub>4</sub>/TMS): δ 0.85–1.90(m, 32 H), 3.97(d, 2 H, *J* = 6.0 Hz, COOCH<sub>2</sub>), 4.10(t, 2 H, *J* = 6.0 Hz, OCH<sub>2</sub>), 7.10(d, 2 H)/7.93(d, 2 H) (AA'BB', *J* = 8.0 Hz, O–C<sub>6</sub>H<sub>4</sub>–COO), 7.51(d, 2 H)/8.03(d, 2 H) (AA'BB', *J* = 8.0 Hz, C≡C–C<sub>6</sub>H<sub>4</sub>–COO); <sup>19</sup>F NMR(CCl<sub>4</sub>/TFA): δ 60.30(m, 2 F, F<sub>arom</sub>), 79.97(m, 2 F, F<sub>arom</sub>); IR(KBr): 2950, 2830, 1740, 1720, 1602, 1518, 1500, 1490, 1442, 1405, 1390, 1260, 1198, 1164, 1105, 1066, 1015, 980, 890, 855, 760, 690 cm<sup>-1</sup>; MS *m/z*(rel. int.) 668(M<sup>+</sup>, 1.56), 461(100.00), 293(18.67); Elemental analysis; Found: C 69.96 per cent, H 6.52 per cent, F 11.09 per cent; Calculated for C<sub>39</sub>H<sub>44</sub>F<sub>4</sub>O<sub>5</sub>: C 70.04 per cent, H 6.63 per cent, F 11.36 per cent.

New fluorinated compounds **16–24** were prepared by a similar procedure. All of them had satisfactory elementary analyses and gave appropriate <sup>1</sup>H and <sup>19</sup>F NMR, IR and MS spectral data.

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