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Synthesis and transition temperatures of novel fluorinated chiral liquid crystals containing 1,4-tetrafluorophenylene units

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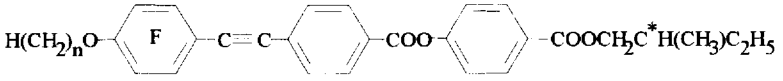
To continue the search for novel series of fluorinated ferroelectric liquid crystals, an additional two series of 4-[(*S*)-2-methylbutoxy]phenyl 4-[(4-*n*-alkoxy-2,3,5,6-tetrafluorophenyl)ethynyl] benzoates (**C**) and 4-(*n*-alkoxy)phenyl 4-[(4-(*S*)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)] benzoates (**D**) have been synthesized. Polarizing microscopic textural observations and DSC measurements of the phase transitions of these novel compounds showed that compounds **C** were liquid crystals with a chiral nematic (N*) phase and a monotropic chiral smectic C phase (S_C^*), and compounds **D** exhibited a chiral nematic (N*) phase.

1. Introduction

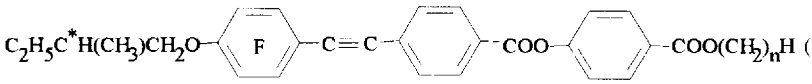
Since the electro-optical properties (fast switching and bistability) of ferroelectric chiral smectic C liquid crystals [1] were first reported by Clark and Lagerwall [2], there has been considerable interest in the synthesis of new chiral smectic C materials. In our earlier papers [3, 4], the following homologous series have been studied:

A



($1<n<9$)

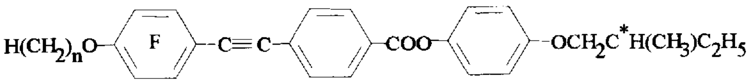
B



($2<n<8$)

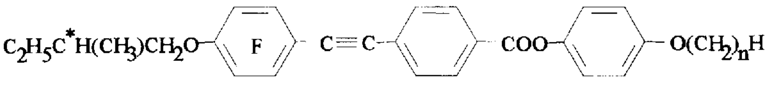
Most of the compounds were shown to exhibit a chiral smectic C phase. It is well known that the systematic substitution of fluorine for hydrogen in mesogenic materials has a remarkable effect on the liquid crystal transition temperatures and other physical properties. For example, the appropriate fluorine-substitution is able to (*a*) increase the stability of the smectic C (S_C) mesophase whilst destabilizing the smectic A (S_A) mesophase [5, 6], (*b*) suppress and eliminate the more ordered smectic mesophases [5, 7], and (*c*) influence the dielectricanisotropy, viscosity, birefringence and melting point [5, 7]. Consequently, hundreds of liquid crystalline materials with monofluoro-, difluoro-, or perfluoro-substituted aromatic rings have been prepared [8–11]. Nevertheless, few liquid crystalline materials with 1,4-disubstituted-tetrafluorobenzene rings [12–20] have been reported. Our goal was, therefore, the synthesis of new liquid crystal compounds with the 2,3,5,6-tetrafluoro-1,4-phenylene moiety in the core with the aim of producing new materials suitable for use in display devices and other applications [21]. We have now prepared these new homologous series **C** and **D** using 1-pentafluorophenyl-2-trimethylsilylacetylene as the starting material. In this paper we report on the synthesis, characterization and transition data of the novel series **C** and **D**.

C



($1<n<9$)

D



($1<n<8$)

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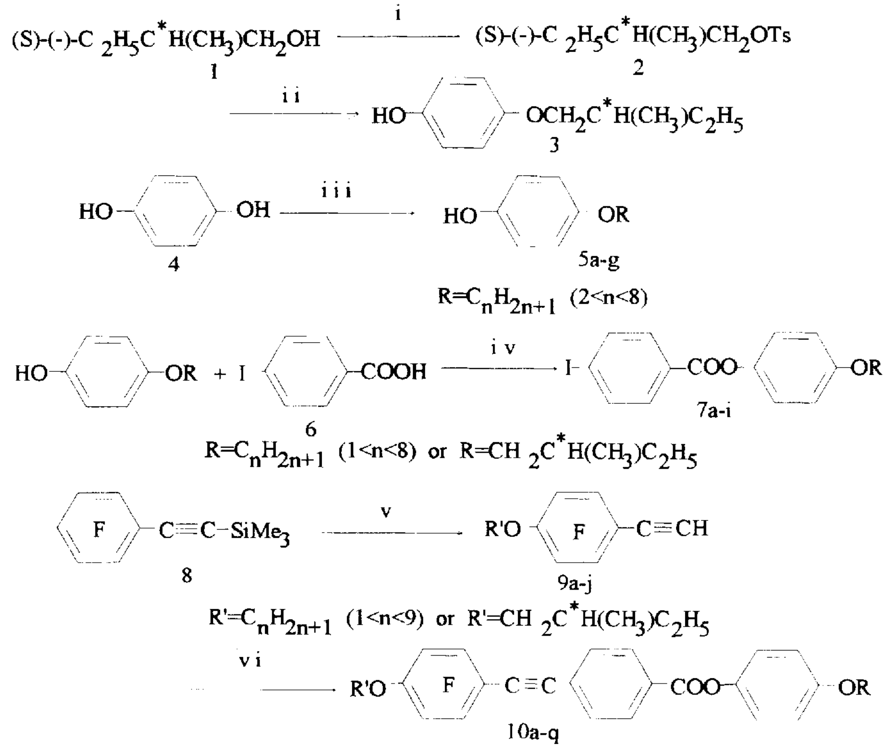
2. Experimental

IR spectra were recorded on a Shimadzu IR-440 spectrophotometer. ^{1}H NMR spectra with TMS as the internal standard and ^{19}F NMR spectra with TFA as the 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.

Two new series **C** and **D** were prepared as shown in the scheme. Full synthetic details and other physical data are available in [22].

*(S)-2-Methylbutyl-*p*-toluenesulphonate* (**2**)

This was prepared from the esterification reaction [23] between toluene sulphonic chloride and (*S*)-2-methylbutanol in anhydrous pyridine. The rection of compound **2** with hydroquinone yielded (*S*)-2-methylbutyloxyphenol (**3**). In the above reactions the configuration of the chiral carbon atom was preserved. The *p*-alkoxyphenols (**5 a–g**) were prepared by a Williamson-type alkylation of hydroquinone [24, 25]. The alkoxyphenyl 4-iodobenzoates (**7 a–i**) were prepared from a mild esterification [26] between 4-iodobenzoic acid and compound **3** or compounds (**5 a–g**) in the presence of both dicyclohexylcarbodimide (DCC) and 4-pyrrolidinopyridine (PPY) as catalyst in dried ether. 1-Pentafluorophenyl-2-trimethylsilyacetylene (**8**) was synthesized by a palladium-catalysed coupling reaction [27] between 1-pentafluoroiodobenzene and trimethylsilylacetylene. The 4-alkoxy-2,3,5,6-tetrafluorophenylacetylenes (**9 a–j**) were easily obtained by the nucleophilic substitution [28] of *n*-alkyl alcohol or (*S*)-2-methylbutanol on compound **8** at room temperature using K_2CO_3 as base. Finally the coupling reaction between compounds **7 a–i** and **9 a–j** under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in dried triethylamine gave the desired polyfluorinated substituted homologous compounds (**10 a–q**).



Series **C**: R=$CH_2C^*H(CH_3)C_2H_5$, R'=C_nH_{2n+1} $(1<n<9)$
Series **D**: R'=$CH_2C^*H(CH_3)C_2H_5$, R=C_nH_{2n+1} $(1<n<8)$
Scheme 1. (i) pyridine, *p*-toluene sulphonic chloride;
(ii) hydroquinone, EtOH, H_2O, KOH, reflux;
(iii) $H(CH_2)_nBr$, EtOH, KOH, reflux;
(iv) DCC, PPY,Et_2O, R.T.;
(v) K_2CO_3, DMF, $H(CH_2)_nOH$;
(vi) compound 7, $[(C_6H_5)_3P]_2PdCl_2$, CuI, Et_3N, reflux.

4-[(S)-2-Methylbutoxy]phenyl 4-[(4-methoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**10a**)

A typical procedure: under dry nitrogen, to a mixture of (*S*)-2-methylbutoxyphenyl 4-iodobenzoate (300 mg, 0·73 mmol), 4-methoxy-2,3,5,6-tetrafluorophenylacetylene (164 mg, 1·11 mmol), bis(triphenylphosphine)palladium dichloride (40 mg, 0·057 mmol) and copper(I) iodide (20 mg, 0·105 mmol) was added 15 ml of anhydrous trithylamine. The resulting mixture was stirred at reflux for 4 h. TLC analysis revealed a complete reaction. The resulting precipitate was filtered off, extracted with ether, the filtrate washed with water, and then dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure with a rotary evaporator and the residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (50:1) as eluent to yield pale yellow crystals. Recrystallization from acetone–methanol gave white flaky crystals of compound (**10a**). Yield: 322 mg (90·7 per cent). ^{1}H NMR (CDCl$_3$): δ 0·66–2·00 (m, 9 H), 3·66 (d, 2 H, J = 5·4 Hz), 4·12 (s, 3 H), 6·82/7·04 (AA′BB′, 4 H, J = 8·4 Hz), 7·62/8·16 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·40 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1495, 1435, 1400, 1265, 1242, 1190, 1125, 1075, 1005, 980, 850, 760, 690 cm^{-1}; MS (*m*/*z*): 486 (M^+), 307 (100·00); Elemental analysis calculated for $C_{27}H_{22}F_4O_4$: C, 66·67; H, 4·53; F,15·64 per cent; Found: C, 66·52; H, 4·53; F, 15·60 per cent.

The compounds **10b–q** were prepared by a similar procedure to that described above for **10a**.

4-[(S)-2-Methylbutoxy]phenyl 4-[(4-ethoxy-2,3,5,6-tetrafluorophenyl)ethynyl[benzoate (**10b**)

^{1}H NMR (CDCl$_3$): δ 0·60–2·04 (m, 12 H), 3·70 (d, 2 H, J = 5·4 Hz), 4·20 (q, 2 H, J = 5·4 Hz), 6·82/7·04 (AA′BB′, 4 H, J = 8·4 Hz), 7·62/8·16 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·40 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1490, 1440, 1395, 1270, 1242, 1200, 1125, 1080, 1010, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 500 (M^+), 321 (100·00); Elemental analysis calculated for $C_{28}H_{24}F_4O_4$: C, 67·20; H, 4·80; F, 15·20 per cent; Found: C, 67·10; H, 4·83; F, 14·95 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-propoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10c**)

^{1}H NMR (CDCl$_3$): δ 0·64–2·04 (m, 14 H), 3·72 (d, 2 H, J = 5·4 Hz), 4·22 (t, 2 H, J = 5·4 Hz), 6·82/7·04 (AA′BB′, 4 H, J = 8·4 Hz), 7·62/8·16 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·40 (m, 2 F), 79·28 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1490, 1440, 1395, 1270, 1242, 1200, 1125, 1080, 1010, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 514 (M^+), 335 (100·00); Elemental analysis calculated for $C_{29}H_{26}F_4O_4$: C, 67·70; H, 5·06; F, 14·79 per cent; Found: C, 67·69; H, 5·05; F, 14·80 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-butoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10d**)

^{1}H NMR (CDCl$_3$): δ 0·60–2·08 (m, 16 H), 3·72 (d, 2 H, J = 5·4 Hz), 4·28 (t, 2 H, J = 5·4 Hz), 6·84/7·08 (AA′BB′, 4 H, J = 8·4 Hz), 7·62/8·16 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·40 (m, 2 F), 79·28 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1480, 1440, 1390, 1260, 1240, 1180, 1125, 1075, 1005, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 528 ($M^+ - 1$), 350 (100·00); Elemental analysis calculated for $C_{30}H_{28}F_4O_4$: C, 68·18; H, 5·30; F, 14·39 per cent; Found: C, 68·01; H, 5·29; F, 14·25 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10e**)

^{1}H NMR (CDCl$_3$): δ 0·72–2·08 (m, 18 H), 3·78 (d, 2 H, J = 5·4 Hz), 4·30 (t, 2 H, J = 5·4 Hz). 6·88/7·20 (AA′BB′, 4 H, J = 8·4 Hz), 7·68/8·18 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·60 (m, 2 F), 79·40 (m, 2 F); IR (KBr): 2920, 1730, 1600, 1490, 1440, 1390, 1270, 1245, 1190, 1125, 1080, 1010, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 542 ($M^+ - 1$), 364 (100·00); Elemental analysis calculated for $C_{31}H_{30}F_4O_4$: C, 68·63; H, 5·54; F, 14·02 per cent; Found: C, 68·49; H, 5·53; F, 14·01 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-hexyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10f**)

^{1}H NMR (CDCl$_3$): δ 0·64–2·02 (m, 20 H), 3·72 (d, 2 H, J = 5·4 Hz), 4·20 (t, 2 H, J = 5·4 Hz), 6·82/7·06 (AA′BB′, 4 H, J = 8·4 Hz), 7·62/8·10 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·60 (m, 2 F), 79·40 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1490, 1440, 1395, 1265, 1245, 1190, 1130, 1080, 1005, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 556 (M^+), 377 (100·00); Elemental analysis calculated for $C_{32}H_{32}F_4O_4$: C, 69·06; H, 5·76; F, 13·67 per cent; Found: C, 68·96; H, 5·75; F, 13·57 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10g**)

^{1}H NMR (CDCl$_3$): δ 0·64–2·04 (m, 22 H), 3·72 (d, 2 H, J = 5·4 Hz), 4·22 (t, 2 H, J = 5·4 Hz), 6·84/7·08 (AA′BB′, 4 H, J = 8·4 Hz), 7·64/8·12 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·60 (m, 2 F), 79·20 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1490, 1440, 1385, 1260, 1250, 1190, 1130, 1075, 1005, 980, 860, 760, 690 cm^{-1}; MS (*m*/*z*): 570 ($M^+ - 1$), 391 (100·00); Elemental analysis calculated for $C_{33}H_{34}F_4O_4$: C, 69·47; H, 5·96; F, 13·33 per cent; Found: C, 69·33; H, 5·90; F, 13·25 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10h**)

^{1}H NMR (CDCl$_3$): δ 0·62–2·06 (m, 24 H), 3·74 (d, 2 H, J = 5·4 Hz), 4·24 (t, 2 H, J = 5·4 Hz), 6·82/7·10 (AA′BB′, 4 H, J = 8·4 Hz), 7·66/8·14 (AA′BB′, 4 H, J = 8·4 Hz); ^{19}F NMR (CDCl$_3$): δ 59·62 (m, 2 F), 79·28 (m, 2 F); IR

(KBr): 2900, 1730, 1600, 1490, 1440, 1380, 1260, 1250, 1190, 1130, 1070, 1005, 980, 860, 760, 690 cm^{-1}; MS (*m/z*): 584 (M$^{+}-1$), 406 (100·00); Elemental analysis calculated for $C_{34}H_{36}F_4O_4$: C, 69·86; H, 6·16; F, 13·01 per cent; Found: C, 69·71; H, 6·09; F, 12·96 per cent.

*4-[(S)-2-Methylbutoxy]phenyl 4-[(4-*n*-nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate* (**10 i**)

^{1}H NMR ($CDCl_3$): δ 0·64–2·04 (m, 14 H), 3·72 (d, 2 H, *J* = 5·4 Hz), 4·28 (t, 2 H, *J* = 5·4 Hz), 6·80/7·08 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·68/8·16 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·64 (m, 2 F), 79·30 (m, 2 F); IR (KBr): 2900, 1730, 1600, 1490, 1440, 1390, 1270, 1240, 1190, 1130, 1070, 1010, 980, 855, 760, 690 cm^{-1}; MS (*m/z*): 598 (M^{+}), 420 (100·00); Elemental analysis calculated for $C_{35}H_{38}F_4O_4$: C, 70·23; H, 6·35; F, 12·71 per cent; Found: C, 70·03; H, 6·29; F, 12·63 per cent.

4-Methyloxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**10 j**)

^{1}H NMR ($CDCl_3$): δ 0·72–2·20 (m, 9 H), 3·80 (s, 3 H), 4·10 (d, 2 H, *J* = 5·4 Hz), 6·92/7·20 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·67/8·18 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·40 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2920, 1730, 1600, 1490, 1440, 1390, 1260, 1250, 1200, 1125, 1075, 980, 850, 760, 690 cm^{-1}; MS (*m/z*): 486 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{27}H_{22}F_4O_4$: C, 66·67; H, 4·53; F, 15·64 per cent; Found: C, 66·68; H, 4·34; F, 15·42 per cent.

4-Ethoxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**10 k**)

^{1}H NMR ($CDCl_3$): δ 0·70–2·20 (m, 12 H), 3·95 (q, 2 H, *J* = 5·4 Hz), 4·07 (d, 2 H, *J* = 5·4 Hz), 6·893/7·23 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·70/8·22 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·40 (m, 2 F), 79·34 (m, 2 F); IR (KBr): 2940, 1740, 1600, 1490, 1440, 1390, 1270, 1250, 1200, 1128, 1080, 982, 855, 765, 690 cm^{-1}; MS (*m/z*): 500 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{28}H_{24}F_4O_4$: C, 67·20; H, 4·80; F, 15·20 per cent; Found: C, 66·96; H, 4·82; F, 15·01 per cent.

*4-Propoxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-*tetrafluorophenyl)ethynyl]benzoate (**10 l**)

^{1}H NMR ($CDCl_3$): δ 0·70–2·20 (m, 14 H), 3·90 (t, 2 H, *J* = 5·4 Hz), 4·05 (d, 2 H, *J* = 5·4 Hz), 6·93/7·23 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·70/8·22 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·50 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2950, 1730, 1600, 1490, 1440, 1390, 1265, 1240, 1192, 1120, 1080, 980, 850, 760, 690 cm^{-1}; MS (*m/z*): 514 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{29}H_{26}F_4O_4$: C, 67·70; H, 5·06; F, 14·79 per cent; Found: C, 67·59; H, 5·10; F, 14·61 per cent.

*4-Butoxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-*tetrafluorophenyl)ethynyl]benzoate (**10 m**)

^{1}H NMR ($CDCl_3$): δ 0·72–2·22 (m, 14 H), 3·72 (t, 2 H, *J* = 5·4 Hz), 4·28 (d, 2 H, *J* = 5·4 Hz), 6·98/7·27 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·66/8·17 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·40 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2920, 1730, 1600, 1490, 1440, 1390, 1260, 1250, 1190, 1120, 1070, 980, 855, 760, 685 cm^{-1}; MS (*m/z*): 528 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{30}H_{28}F_4O_4$: C, 68·18; H, 5·30; F, 14·39 per cent; Found: C, 68·22; H, 5·22; F, 14·45 per cent.

*4-Pentyloxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-*tetrafluorophenyl)ethynyl]benzoate (**10 n**)

^{1}H NMR ($CDCl_3$): δ 0·70–2·20 (m, 18 H), 3·95 (t, 2 H, *J* = 5·4 Hz), 4·10 (d, 2 H, *J* = 5·4 Hz), 6·90/7·30 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·66/8·17 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·40 (m, 2 F), 79·30 (m, 2 F); IR (KBr): 2920, 1730, 1600, 1495, 1440, 1395, 1270, 1250, 1200, 1125, 1080, 980, 860, 765, 690 cm^{-1}; MS (*m/z*): 542 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{31}H_{30}F_4O_4$: C, 68·63; H, 5·54; F, 14·02 per cent; Found: C, 68·55; H, 5·32; F, 14·10 per cent.

4-Hexyloxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**10 o**)

^{1}H NMR ($CDCl_3$): δ 0·70–2·20 (m, 20 H), 3·95 (t, 2 H, *J* = 5·4 Hz), 4·09 (d, 2 H, *J* = 5·4 Hz), 6·93/7·20 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·70/8·21 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·50 (m, 2 F), 79·30 (m, 2 F); IR (KBr): 2920, 1735, 1600, 1495, 1440, 1390, 1270, 1250, 1195, 1120, 1075, 980, 860, 760, 690 cm^{-1}; MS (*m/z*): 556 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{32}H_{32}F_4O_4$: C, 69·06; H, 5·76; F, 13·67 per cent; Found: C, 68·95; H, 5·80; F, 13·71 per cent.

4-Heptyloxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-tetrafluorophenyl)ethynyl]benzoate (**10 p**)

^{1}H NMR ($CDCl_3$): δ 0·72–2·20 (m, 22 H), 3·90 (t, 2 H, *J* = 5·4 Hz), 4·10 (d, 2 H, *J* = 5·4 Hz), 6·97/7·25 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·74/8·23 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·40 (m, 2 F), 79·32 (m, 2 F); IR (KBr): 2920, 1735, 1600, 1495, 1440, 1390, 1265, 1250, 1190, 1120, 1075, 980, 850, 760, 690 cm^{-1}; MS (*m/z*): 570 (M^{+}), 363 (100·00); Elemental analysis calculated for $C_{33}H_{34}F_4O_4$: C, 69·47; H, 5·96; F, 13·33 per cent; Found: C, 69·60; H, 5·94; F, 13·16 per cent.

*4-Octyloxyphenyl 4-[(4-(S)-2′-methylbutoxy-2,3,5,6-*tetrafluorophenyl)ethynyl]benzoate (**10 q**)

^{1}H NMR ($CDCl_3$): δ 0·70–2·20 (m, 24 H), 3·95 (t, 2 H, *J* = 5·4 Hz), 4·07 (d, 2 H, *J* = 5·4 Hz), 6·93/7·20 (AA′BB′, 4 H, *J* = 8·4 Hz), 7·70/8·23 (AA′BB′, 4 H, *J* = 8·4 Hz); ^{19}F NMR ($CDCl_3$): δ 59·42 (m, 2 F), 79·32 (m, 2 F); IR

(KBr): 2920, 1740, 1600, 1495, 1440, 1390, 1270, 1250, 1195, 1122, 1075, 980, 860, 760, 690 $\mathrm{cm^{-1}}$; MS (*m*/*z*): 584 (M^+), 363 (100·00); Elemental analysis calculated for $C_{34}H_{36}F_4O_4$: C, 69·86; H, 6·16; F, 13·01 per cent; Found: C, 69·90; H, 6·08; F, 13·11 per cent.

3. Results and discussion

The mesomorphic properties were determined using a Mettler FP 52 hot stage, Mettler FP 5 temperature controller and an Olympus BH-2 polarizing microscope. Phase identification was made by comparing the observed textures with those in the literature [29, 30]. All of the new compounds were studied by differential scanning calorimetry using a Perkin–Elmer DSC 7 calorimeter. All the compounds gave satisfactory analyses.

3.1. *Optical microscopy studies*

The transitional properties of the chiral compounds of series **C** are summarized in table 1. Figure 1 shows a plot of the transition temperatures as a function of the alkoxy chain length (*n*) of series **C**. There is no discernible regular trends in the transition temperatures as the alkoxy chain length increases. Only compounds **10 f**, **10 h**, **10 i** exhibit a monotropic S_C^* phase. At first, we thought it was a problem of purity but repeated careful purifications lead to the same transition temperatures.

From the comparison between the transition temperatures of series **A** [3] and **C**, we note that the compounds of series **C** tend to have higher melting points and lower clearing points than the equivalent homologue of series **A** with the same terminal *n*-alkoxy chain. Furthermore, the compounds of series **A** exhibit both the chiral smectic C phase (monotropic and enantiotropic) and smectic A phase whereas the series **C** compounds do not possess the smectic A phase and only three show the monotropic smectic C phase. It appears that the presence of an alkoxy group in place of the carboxylate group in the optically active alkyl chain significantly changes the liquid crystal phase and transition temperatures.

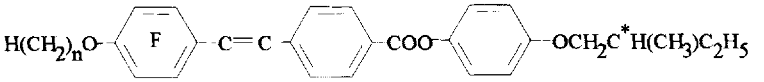
The compounds of series **D** have the chemical structure in which the two terminal substituents of series **C** are exchanged. The major difference between the **D** and **C** series is that the chiral alkoxy group is conjugated with the phenylene ring in series **C**, but not in series **D**. The transitional properties of series **D** are shown in table 2 and the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (*n*) in figure 2. All eight compounds of series **D** are liquid crystalline exhibiting the enantiotropic chiral nematic phase. The N*–I transitions show the classic odd–even effect which attenuates with increasing terminal chain length *n*. The melting points show no regular trend. A comparison of the transition temperatures of these compounds with the transition temperatures of series **C** reveals that the melting points and the clearing points of series **D** are on average higher. The thermostabilities are greater than series **C** and they do not exhibit the S_C^* phase. It appears important that in order to exhibit the S_C^* phase the chiral and carboxylate groups must be positioned near to each other in this type of fluorinated structure.

3.2. *Differential scanning calorimetric studies*

This study was performed with a Perkin–Elmer DSC 7. The results are given in tables 1 and 2.

The melting enthalpies for compounds **10 a–i** vary from 22·20 to 35·06 $\mathrm{kJ\,mol^{-1}}$ and the average value is 30·84 $\mathrm{kJ\,mol^{-1}}$. For compounds **10 j–q** the values vary from 22·74 to 48·48 $\mathrm{kJ\,ol^{-1}}$ and average 31·02 $\mathrm{kJ\,mol^{-1}}$.

Table 1. Transition temperatures (°C) and enthalpies ($\mathrm{kJ\,mol^{-1}}$) [in square brackets] of series **C**.



Compound	*n*	Transition data			
		Cr	S_C^*	N*	I
10 a	1	● 81·3[23·24]		● 148·8[0·31]	●
10 b	2	● 91·8[31·37]		● 166·8[0·46]	●
10 c	3	● 108·1[25·47]		● 160·1[0·26]	●
10 d	4	● 98·7[22·20]		● 162·2[0·57]	●
10 e	5	● 102·4[28·22]		● 150·6[0·46]	●
10 f	6	● 81·4[33·13]	● (78·1)[0·51]	● 136·3[0·54]	●
10 g	7	● 98·6[26·88]		● 137·8[0·41]	●
10 h	8	● 85·6[35·06]	● (82·0)[0·59]	● 136·3[0·60]	●
10 i	9	● 82·2[26·65]	● (82·1)[0·67]	● 131·3[0·62]	●

Parentheses denote a monotropic transition.

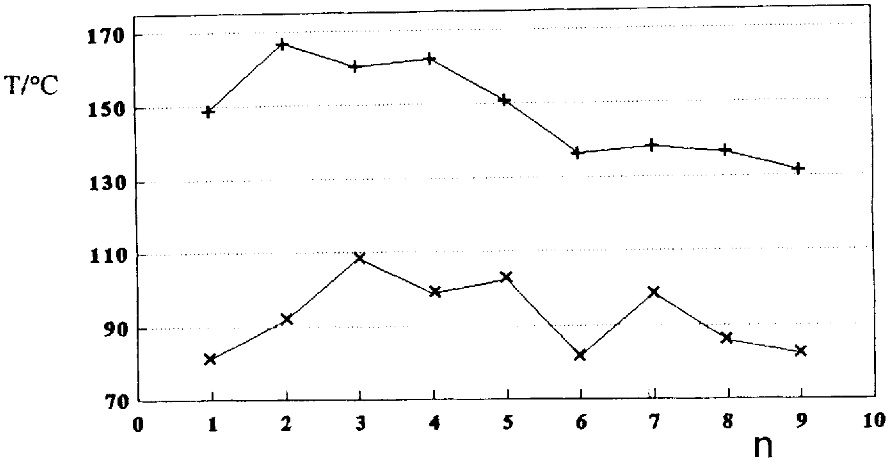
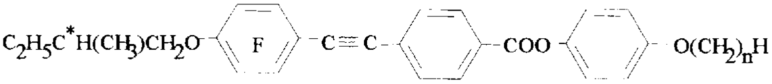


Figure 1. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkoxy chain for series **C**. Melting points are denoted by × and the chiral nematic to isotropic phase transitions by +.

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) [in square brackets] of series D.



		Transition temperature/°C [kJ/Mol]		
Compound	*n*	Cr	N*	I
10j	1	● 107·3[48·48]	● 178·5[0·55]	●
10k	2	● 95·8[23·55]	● 193·3[0·71]	●
10l	3	● 107·8[22·74]	● 171·0[0·54]	●
10m	4	● 107·2[30·26]	● 173·7[0·67]	●
10n	5	● 110·3[30·36]	● 163·4[0·71]	●
10o	6	● 107·1[28·42]	● 164·5[0·71]	●
10p	7	● 106·5[35·02]	● 160·9[0·86]	●
10q	8	● 112·2[29·30]	● 157·4[0·41]	●

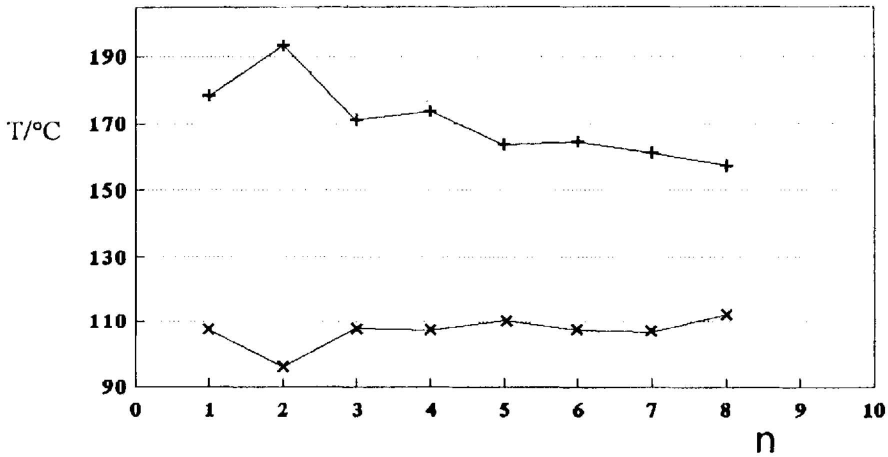


Figure 2. Plot of transition temperatures against the number of carbon atoms (*n*) in the alkoxy chain for series **D**. Melting points are denoted by × the chiral nematic to isotropic phase transitions by +.

The N*–I transition enthalpies for compounds **10a–i** are approximately 0·47 kJ mol^{-1}, and for compounds **10j–q** are about 0·65 kJ mol^{-1}. From the comparison between the transition enthalpies of series **C** and **D** we note that the average values of the melting enthalpies for two series compounds are similar. However, the N*–I transition enthalpies for series **D** are slightly larger than for series **C**.

4. Conclusions

Two homologous series of fluorinated chiral liquid crystals were prepared via a Pd-catalysed coupling reaction. The chiral nematic phase, as well as a monotropic S_C^* phase, is observed in series **C**. Series **D** exhibits only the N* mesophase. A comparison of the data of series **A**/**B** and series **C**/**D** revealed that the presence of the alkoxy group in the place of the carboxylate group in this type of the fluorinated structure destabilizes the smectic mesophases.

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