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Synthesis and mesomorphic properties of some fluorinated phenyl 4-[(4-*n*-alkoxyphenyl)ethynyl]benzoates

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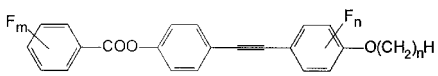
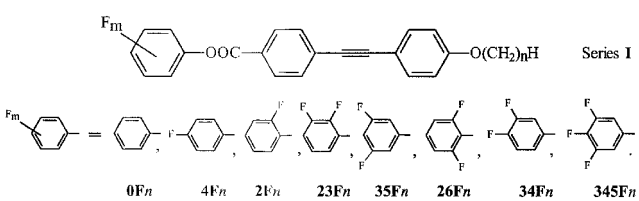
Eight homologous series of fluorinated phenyl 4-[(4-*n*-alkoxyphenyl)ethynyl]benzoates have been synthesized. Textural observations by polarizing microscopy and DSC measurements of the phase transitions show that most of these compounds are thermotropic liquid crystals with nematic and smectic A phases; furthermore, several show monotropic high order smectic phases. The results showed that the SmA phase is enhanced with increasing degree of fluoro-substitution on the *para*- and *meta*-positions of the terminal phenyl groups. The mesomorphic properties of these compounds are also affected by the direction of ester bonds. The effect of triple bonds is also discussed.

1. Introduction

Fluorinated liquid crystals are a focus of research in the liquid crystal (LC) field. The fluoro substituent is ideal in that it comibines the properties of large electronegativity and small size so that it significantly affects the physical properties of molecules without eliminating the possibility of mesophase formation. Many patents have been published on systems with fluoro substituents in the terminal phenyl ring, and terminal fluoro-substituted LCs have been widely used in nematic mixtures for TFT applications. Although hundreds of LC compounds with fluoro-substituted phenyl groups have been prepared, and the effect of lateral fluoro-substitution in LCs is well reported and summarized [1–12], the fact that not only *para*- but also *meta*-fluoro substitution on the terminal phenyl group enhances the formation of the SmA phase in the series shown below is now well studied [13–15].



To study this phenomenon further, eight series of compounds were synthesized by changing the ester bond direction of these compounds. The structures of compounds synthesized in this study are shown below.



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2. Experimental

2.1. *Characterization*

All of the product compounds were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent and then recrystallized from acetone/methanol.

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. ^{1}H NMR spectra with TMS as internal NMR standard were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz), and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM 360L spectrometer (56.4 MHz). For ^{19}F NMR spectra the high field was positive. Ms spectra were measured with a Finnigan-4021 spectroscope.

The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces.

2.2. *Synthesis*

The synthesis of the target molecules is outlined in scheme 1. The compound **8** and other fluorinated phenols were easily obtained by the published procedure [16]. The compounds **15** were then synthesized via a

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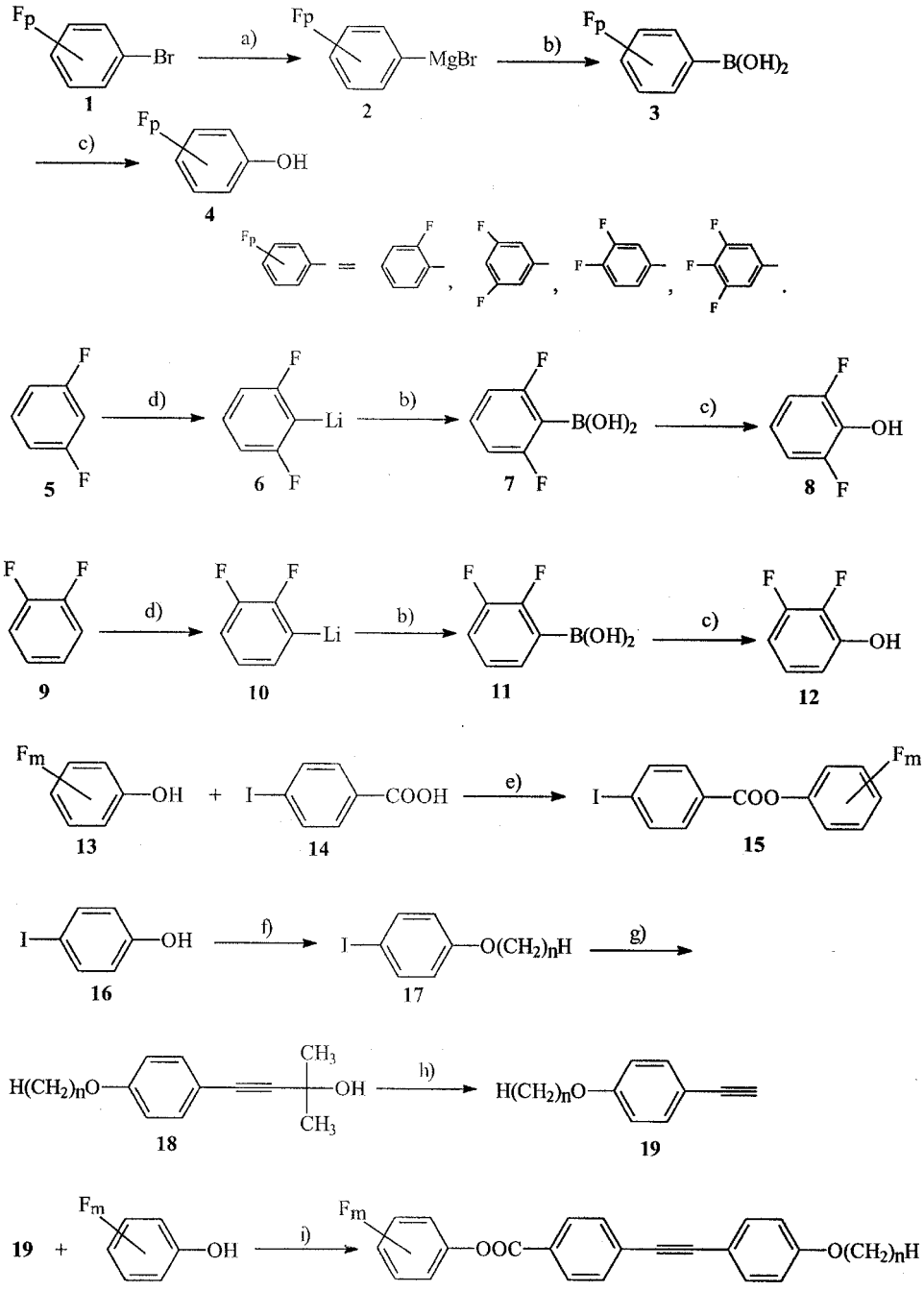


Reagents and conditions: (*a*) Mg, $CH_3CH_2OCH_2CH_3$; (*b*) $B(OMe)_3$, H_3^+O; (*c*) H_2O_2; (*d*) LiBu, heptane; (*e*) DCC/DMAP, THF; (*f*) $C_nH_{2n+1}Br$/NaOH, C_2H_5OH/H_2O; (*g*) CuI, PPh_3, $HOC(CH_3)_2C{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, THF/Et_3N; (*h*) KOH, $C_6H_5CH_3$; (*i*) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N.

Scheme 1. Synthesis route.

mild one-pot esterification procedure, between **13** and **14** in the presence of both dicyclohexylcarbodiimide (DCC) and DMAP catalyst in dried tetrahydrofuran (THF). Compounds **17** were obtained by etherification of 4-iodophenol and bromoalkanes. Compounds **18** were synthesized by the coupling reaction of 2-methyl-3-butyn-2-ol with aryl iodides **17**. The compounds **19** were then obtained by deprotection of the aryl acetylides

18 [17]. Finally the coupling reaction between compounds **13** and **19** under the catalysis of bis(triphenylphosphine)palladium dichloride, triphenylphosphine and copper(I) iodide in dried triethylamine and THF gave the target compounds. Representative synthesis details and characterization data are given below.

2.2.1. *2,6-Difluorophenol (**8**)*

Butyllithium (1.6 mol/l in hexane, 33 ml, 52.8 mmol) was added dropwise to a stirred, cooled (−78°C) solution of compound **5** (5.8 g, 46.3 mmol) in dry THF (65 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 2.5 h and then a previously cooled solution of trimethyl borate (10.4 g, 100.0 mmol) in dry THF (25 ml) was added dropwise at −78°C. The reaction mixture was allowed to warm to r.t. overnight and then stirred for 1 h with 10% hydrochloric acid (30 ml). The product was extracted into ether (twice); the combined ethereal extracts were then washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a white powder (8.0 g). 10% Hydrogen peroxide (10%, 50 ml, 146.7 mmol) was added dropwise to a stirred solution of the white powder in ether (50 ml) heated under reflux. The stirred mixture was heated under reflux for 2.5 h and cooled. The ether layer was separated and the aqueous layer washed with ether. The combined ethereal layers were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by flash chromatography to give colourless crystals; yield 5.59 g, 85.3%. δ_F ($CDCl_3$): 59.1 (s, 2F) ppm. *M/z* (%): 130 (100.00), 82 (55.78), 110 (23.32).

2.2.2. *4-Fluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**4F8**)*

Anhydrous triethylamine (15 ml) was added under dry nitrogen to a mixture of 4-*n*-octoxyphenylacetylene (230 mg, 1.00 mmol), 4-fluorophenyl 4-iodiobenzoate (308 mg, 0.90 mmol), bis(triphenylphosphine)palladium dichloride (30 mg) and copper(I) iodide (50 mg). The resulting mixture was heated under reflux with stirring. Analysis by TLC revealed completion of the reaction within 8 h. The precipitate formed was then filtered off and the solvent removed *in vacuo*. The residue was purified by flash chromatography and recrystallized from acetone–methanol to give a white solid; yield 300 mg, 75.1%. IR (KBr) ν_{max}: 2920, 2853, 2216, 1738, 1599, 1256, 1203, 844 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.93–1.85 (m, 15H, aliphatic hydrogens), 3.96 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.72–8.30 (m, 12H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 39.70 (s, F) ppm. MS *m/z* (rel. int.): 444 (M^+, 8.91), 332 ($C_8H_{17}OC_6H_4{-}{\equiv}{-}C_6H_4CO^+ - 1$, 100.00), 221 ($HOC_6H_4{-}{\equiv}{-}C_6H_4CO^+$, 11.22). Anal: calcd $C_{29}H_{29}FO_3$, C 78.35, H 6.58, F 4.27; found C 78.24, H 6.67, F 4.31%.

2.2.3. *Phenyl 4-[(4-n-octoxyphenyl)ethynyl]benzoate (**0F8**)*

IR (KBr) ν_{max}: 2920, 2853, 2215, 1737, 1597, 1514, 1405, 1253, 1179, 858, 830 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.91 (t, $J = 6.6$ Hz, 3H, CH_3), 1.31–1.85 (m, 12H, $6 \times CH_2$), 3.98 (t, $J = 6.6$ Hz, 2H, RCH_2O), 6.90 (d, $J = 6.7$ Hz, 2H, ArH), 7.23–7.32 (m, 3H, ArH), 7.43–7.53 (m, 4H, ArH), 7.63–7.66 (m, 2H, ArH), 8.17–8.20 (m, 2H, ArH) ppm. MS *m/z* (rel. int.): 426 (M^+, 10.23), 332 ($C_8H_{17}OC_6H_4{-}{\equiv}{-}C_6H_4CO^+ - 1$, 100.00). Anal: calcd for $C_{29}H_{30}O_3$, C 81.66, H 7.09; found C 81.69, H 7.16%.

2.2.4. *2-Fluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**2F8**)*

IR (KBr) ν_{max}: 2921, 2852, 2213, 1745, 1598, 1566, 1467, 1258, 1180, 859, 842 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.26–1.86 (m, 12H, $6 \times CH_2$), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.83–6.93 (d, 2H, ArH), 7.20–7.28 (m, 4H, ArH), 7.45–7.67 (m, 4H, ArH), 8.14–8.22 (d, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 51.33 (m, F) ppm. MS *m/z* (rel. int.): 444 (M^+, 5.70), 333 ($C_8H_{17}OC_6H_4{-}{\equiv}{-}6H_4CO^+$, 100.00), 221 ($HOC_6H_4{-}{\equiv}{-}C_6H_4CO^+$, 7.02). Anal: calcd for $C_{29}H_{29}FO_3$, C 78.35, H 6.58, F 4.27; found C 78.17, H 6.51, F 4.39%.

2.2.5. *3,4-Difluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**34F8**)*

IR (KBr) ν_{max}: 2920, 2853, 2215, 1726, 1618, 1566, 1516, 1472, 1253, 1142, 858, 842 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.30–1.90 (m, 12H, $6 \times CH_2$), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.84–7.17 (m, 5H, ArH), 7.45–7.67 (m, 4H, ArH), 8.10–8.19 (d, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 57.70 (m, F), 63.95 (m, F) ppm. MS *m/z* (rel. int.): 462 (M^+, 9.35), 333 ($C_8H_{17}OC_6H_4{-}{\equiv}{-}6H_4CO^+$, 100.00), 221 ($HOC_6H_4{-}{\equiv}{-}C_6H_4CO^+$, 11.04). Anal: calcd for $C_{29}H_{28}F_2O_3$, C 75.31, H 6.10, F 8.21; found C 75.19, H 6.06, F 8.26%.

2.2.6. *3,5-Difluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**35F8**)*

IR (KBr) ν_{max}: 2925, 2856 (s, C−H), 2217 (s, C≡C), 1740 (vs, C=O), 1609 (s, C_6H_4), 1516 (vs, $C_6H_3F_2$), 1268, 1181 (s, C−O−C) cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.91 (t, 3H, CH_3), 1.37–1.79 (m, 12H, $6 \times CH_2$), 3.94 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.65–6.92 (m, 5H, ArH), 7.44–7.68 (m, 4H, ArH), 8.13 (d, $J = 8$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 31.11

(s, F) ppm. MS *m/z* (rel. int.): 462 (M^+, 22.22), 333 (C_8H_{17}–OC_6H_4–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 37.04). Anal: calcd for $C_{29}H_{28}F_2O_3$, C 75.31, H 6.10, F 8.21; found C 75.33, H 6.00, F 8.13%.

2.2.7. *2,6-Difluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**26F**8)*

IR (KBr) ν_{max}: 2920, 2856 (s, C–H), 2210 (s, C≡C), 1740 (vs, C=O), 1596 (s, C_6H_4), 1495 (vs, $C_6H_3F_2$), 1263, 1182 (s, C–O–C) cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.91 (t, 3H, CH_3), 1.37–1.79 (m, 12H, 6 × CH_2), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.83–7.10 (m, 5H, ArH), 7.44–7.68 (m, 4H, ArH), 8.17 (d, $J = 8$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 48.60 (s, F) ppm. MS *m/z* (rel. int.): 462 (M^+, 4.46), 333 (C_8H_{17}–OC_6H_4–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 7.34). Anal: calcd for $C_{29}H_{28}F_2O_3$, C 75.31, H 6.10, F 8.21; found C 75.20, H 6.28, F 8.18%.

2.2.8. *2,3-Difluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**23F**8)*

IR (KBr) ν_{max}: 2923, 2853 (s, C–H), 2214 (s, C≡C), 1735 (vs, C=O), 1598, 1502, 1249, 1178 cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.91 (t, 3H, CH_3), 1.37–1.79 (m, 12H, 6 × CH_2), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.83–7.10 (m, 5H, ArH), 7.44–7.68 (m, 4H, ArH), 8.17 (d, $J = 8$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 58.60 (d, $J = 18.8$ Hz, F), 74.00 (d, $J = 18.8$ Hz, F) ppm. MS *m/z* (rel. int.): 463 ($M^+ + 1$, 8.49), 333 (C_8H_{17}–OC_6H_4–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 12.21). Anal: calcd for $C_{29}H_{28}F_2O_3$, C 75.31, H 6.10, F 8.21; found C 75.49, H 6.11, F 8.25%.

2.2.9. *3,4,5-Trifluorophenyl 4-[(4-n-octoxyphenyl)ethynyl]-benzoate (**345F**8)*

IR (KBr) ν_{max}: 2924, 2856 (s, C–H), 2217 (s, C≡C), 1740 (vs, C=O), 1599 (s, C_6H_4), 1529 (vs, $C_6H_2F_3$), 1248, 1181 (s, C–O–C) cm^{-1}. ^1H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.91 (t, 3H, CH_3), 1.37–1.79 (m, 12H, 6 × CH_2), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.88–7.03 (m, 4H, ArH), 7.44–7.67 (m, 4H, ArH), 8.12 (d, $J = 8$ Hz, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 56.42 (q, $J = 11$ Hz, 8 Hz, 2F), 87.90 (t, $J = 20$ Hz, F) ppm. MS *m/z* (rel. int.): 480 (M^+, 7.73), 333 (C_8H_{17}–OC_6H_4–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 18.02). Anal: calcd for $C_{29}H_{27}F_3O_3$, C 72.49, H 5.66, F 11.86; found C 72.56, H 5.59, F 12.03%.

Table 1. Transition temperatures of series **0F***n*, **4F***n*, **34F***n* and **345F***n*. Cr = Crystal; N = nematic phase; SmA = smectic A phase; SmB = smectic B phase; I = isotropic phase; Recr = Recrystallization.

Compound	*n*	Transition temperature/°C
0F6	6	Cr 111.4 SmA 112.0 N 147.3 I 146.1 N 111.2 SmA 99.5 Recr
0F7	7	Cr 109.1 SmA 115.7 N 142.2 I 141.2 N 114.5 SmA 88.6 Recr
0F8	8	Cr 101.7 SmA 121.3 N 142.4 I 141.4 N 120.2 SmA 85.5 SmB 81.7 Recr
0F9	9	Cr 104.7 SmA 122.6 N 137.3 I 136.2 N 121.1 SmA 85.9 SmB 75.2 Recr
0F10	10	Cr 102.5 SmA 126.2 N 137.7 I 136.7 N 125.3 SmA 87.2 SmB 75.6 Recr
4F6	6	Cr 127.1 SmA 165.5 N 203.0 I 201.4 N 163.5 SmA 108.2 Recr
4F7	7	Cr 115.7 SmA 173.1 N 197.3 I 196.2 N 171.7 SmA 105.1 Recr
4F8	8	Cr 115.0 SmA 176.7 N 194.0 I 192.6 N 175.4 SmA 100.9 Recr
4F10	10	Cr 112.9 SmA 177.9 N 183.9 I 182.8 N 176.4 SmA 93.7 Recr
34F4	4	Cr 132.8 SmA 165.4 N 197.2 I 195.2 N 163.0 SmA 107.9 Recr
34F5	5	Cr 128.7 SmA 168.4 N 185.0 I 186.3 N 167.0 SmA 107.2 Recr
34F6	6	Cr 117.0 SmA 171.3 N 184.0 I 183.0 N 170.0 SmA 96.1 Recr
34F7	7	Cr 103.7 SmA 173.2 N 179.2 I 177.9 N 172.0 SmA 89.3 Recr
34F8	8	Cr 105.7 SmA 174.1 N 176.4 I 175.1 N 172.2 SmA 86.9 Recr
34F9	9	Cr 100.0 SmA 173.4 I 171.1 SmA 83.6 Recr
34F10	10	Cr 103.0 SmA 172.5 I 170.2 SmA 82.3 Recr
34F12	12	Cr 101.8 SmA 168.1 I 166.3 SmA 84.0 Recr
345F4	4	Cr 132.1 SmA 152.3 N 166.4 I 165.1 N 150.6 SmA 98.9 Recr
345F5	5	Cr 119.8 SmA 154.3 N 159.0 I 157.8 N 152.6 SmA 99.9 Recr
345F6	6	Cr 112.8 SmA 162.0 N 163.3 I 161.2 N 160.4 SmA 90.0 Recr
345F7	7	Cr 113.7 SmA 160.5 I 158.8 SmA 86.6 Recr
345F8	8	Cr 105.3 SmA 160.6 I 159.0 SmA 88.9 Recr
345F9	9	Cr 106.0 SmA 157.2 I 155.3 SmA 86.7 Recr
345F10	10	Cr 97.2 SmA 156.1 I 154.1 SmA 79.8 Recr
345F12	12	Cr 105.3 SmA 160.6 I 159.0 SmA 88.9 Recr

3. Results and discussion

The transition temperatures of compounds **0F***n*, **4F***n*, **34F***n*, **345F***n*, **2F***n*, **35F***n*, **23F***n* and **26F***n* are presented in tables 1 and 2. The clearing points of these series are shown in figure 1. With the exception of the **26F***n* series, all of these compounds show enantiotropic N and SmA phases.

The clearing points of all these series show an odd–even effect. Compounds **0F***n*, **4F***n*, **34F***n*, **345F***n* and **23F***n* exhibit enantiotropic nematic and smectic A phases, while compounds **2F***n* show enantiotropic nematic phases and monotropic smectic A phases with longer alkoxy chains. Most of compounds **26F***n* are monotropic liquid crystals. Compounds **35F***n* form smectic phases rather than any other LC phases.

If we consider series **4F***n* and **345F***n* to be, respectively, derivatives of the parent series **0F***n* and **35F***n* with a *para*-fluoro substituent, the latter's length/diameter ratio is lower than that of the former. The clearing points of the compounds **4F***n* and **345F***n* would then be expected to be higher than those of their corresponding parents. This is shown to be the case in figure 1. From this figure, it can also be seen that the clearing points fall with increased degree of *meta*-fluoro substitution.

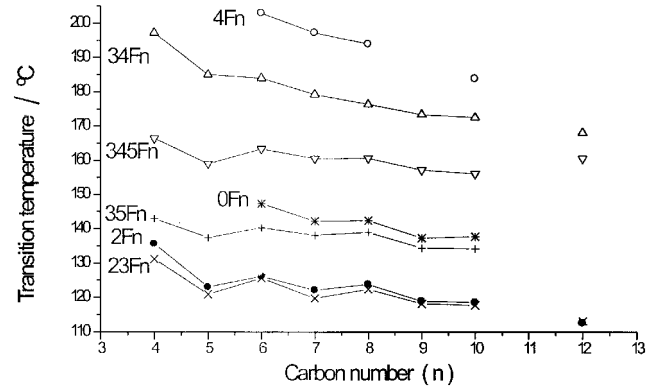


Figure 1. The number of carbon atoms in the alkoxy chain versus the clearing points of the seven series listed in tables 1 and 2.

Table 2. Transition temperatures of series **2F***n*, **35F***n*, **23F***n* and **26F***n*. Cr = Crystal; N = nematic phase; SmA = smectic A phase; SmC = smectic C phase; SmG = smectic G phase; I = isotropic phase; Recr = Recrystallization.

Compound	*n*	Transition temperature/°C
2F4	4	Cr 115.4 N 135.7 I 134.1 N 92.0 Recr
2F5	5	Cr 102.3 N 123.0 I 121.8 N 69.7 SmA 66.9 Recr
2F6	6	Cr 95.2 N 126.1 I 124.6 N 78.8 SmA 69.4 Recr
2F7	7	Cr 95.3 N 122.1 I 120.9 N 80.6 SmA 71.0 Recr
2F8	8	Cr 96.5 N 123.8 I 122.2 N 87.8 SmA 64.4 Recr
2F9	9	Cr 99.5 N 118.9 I 117.7 N 88.8 SmA 70.6 Recr
2F10	10	Cr 91.0 N 118.5 I 117.3 N 91.7 SmA 59.8 Recr
2F12	12	Cr 87.5 SmA 95.1 N 112.6 I 111.3 N 94.0 SmA 66.8 Recr
35F4	4	Cr 115.2 SmA 143.0 I 140.8 SmA 103.8 Recr
35F5	5	Cr 101.7 SmA 137.4 I 135.5 SmA 91.9 Recr
35F6	6	Cr 104.8 SmA 140.3 I 137.9 SmA 95.0 SmC 90.4 Recr
35F7	7	Cr 92.2 SmA 138.1 I 136.4 SmA 91.7 SmC 74.0 SmX 71.0 Recr
35F8	8	Cr 92.5 SmA 139.0 I 136.9 SmA 90.7 SmC 69.6 SmX_a 64.0 SmX_b 62.8 Recr
35F9	9	Cr 94.9 SmA 134.4 I 132.8 SmA 79.0 SmC 64.6 Recr
35F10	10	Cr 94.3 SmA 134.2 I 132.0 SmA 72.5 SmC 68.0 SmG 64.2 Recr
23F4	4	Cr 114.6 N 131.2 I 129.6 N 104.6 SmA 86.2 Recr
23F5	5	Cr 91.0 N 120.9 I 117.3 N 98.6 SmA 86.7 Recr
23F6	6	Cr 91.0 N 125.6 I 117.3 N 105.6 SmA 88.6 Recr
23F7	7	Cr 91.0 N 119.7 I 117.3 N 103.0 SmA 89.1 Recr
23F8	8	Cr 103.1 SmA 110.2 N 122.4 I 121.0 N 108.6 SmA 84.4 Recr
23F9	9	Cr 102.3 SmA 108.7 N 118.1 I 116.3 N 107.1 SmA 81.4 Recr
23F10	10	Cr 101.9 SmA 110.7 N 117.7 I 116.2 N 109.0 SmA 89.0 Recr
23F12	12	Cr 102.4 SmA 110.9 N 113.1 I 111.6 N 108.3 SmA 78.1 Recr
23F16	16	Cr 107.7 I 105.0 SmA 90.5 Recr
26F4	4	Cr 117.4 I 113.9 N 82.3 Recr
26F5	5	Cr 90.8 N 101.1 N 99.9 N 68.8 SmA 65.6 Recr
26F6	6	Cr 106.6 I 105.8 N 93.1 Recr
26F7	7	Cr 107.6 I 100.5 N 90.0 Recr
26F8	8	Cr 112.8 I 103.1 N 95.1 Recr
26F9	9	Cr 91.1 N 98.9 I 97.6 N 76.1 SmA 69.4 Recr
26F10	10	Cr 99.6 I 97.3 N 76.8 SmA 72.1 Recr
26F12	12	Cr 93.4 I 93.0 N 76.5 SmA 70.7 Recr

In the case of series **2F*n***, because of the strong dipole interaction between the *meta*-fluoro substituent and the carboxy group, the carboxy and the phenyl group will not be in the same plane The *ortho*-fluoro substituent will not only broaden but also thicken the molecules. Clearing points are thus much decreased by the fluoro substituent.

It is found that the clearing points of compounds **2F*n*** and those of the corresponding compounds **23F*n*** are similar. This may be because a second lateral fluoro substituent does not broaden the molecule. But as the two fluoro substituents are sited on one side of molecule, their dipoles clearly reinforce and provide strong lateral–lateral attractions; compounds **23F*n*** are thus more prone to smectic phases formation.

In compounds **26F*n***, with a fluoro substituent opposite to the corresponding compounds **2F*n***, the second fluoro substituent broadens the molecule so much that most of compounds **26F*n*** show only monotropic mesophases.

In the tables 1 and 2, we also see that not only the *para*-fluoro substitution on the terminal phenyl group but also the *meta*-fluoro substitution enhances the formation of smectic A phase, as previously reported [13–15]. It seems that a *meta*-fluoro substituent on the terminal phenyl enhances smectic A phase more than the *para*-fluoro substituent. We have previously discussed that this phenomenon may be caused by the occurrence of microphase separation when the number of the fluorine atoms is increased [14].

To study further the formation of LC phases in this type of compound, figures 2 and 3 show the effect of the ester bond direction and of the presence of a triple bond. The structures of the previously reported [13–15] series **I′** and **I″** compounds are shown in scheme 2.

Figure 2 shows that, although these compounds differ only in the direction of the ester bond, compounds **I″**

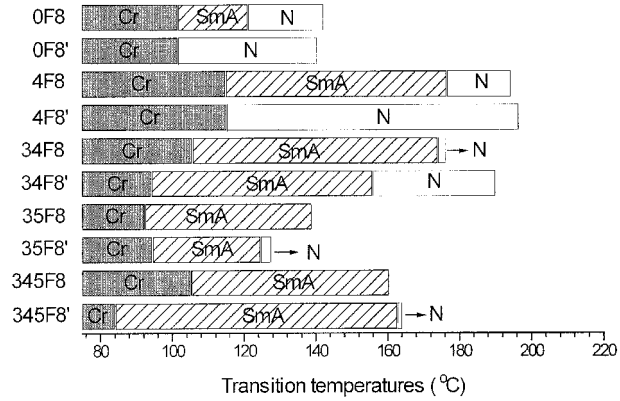
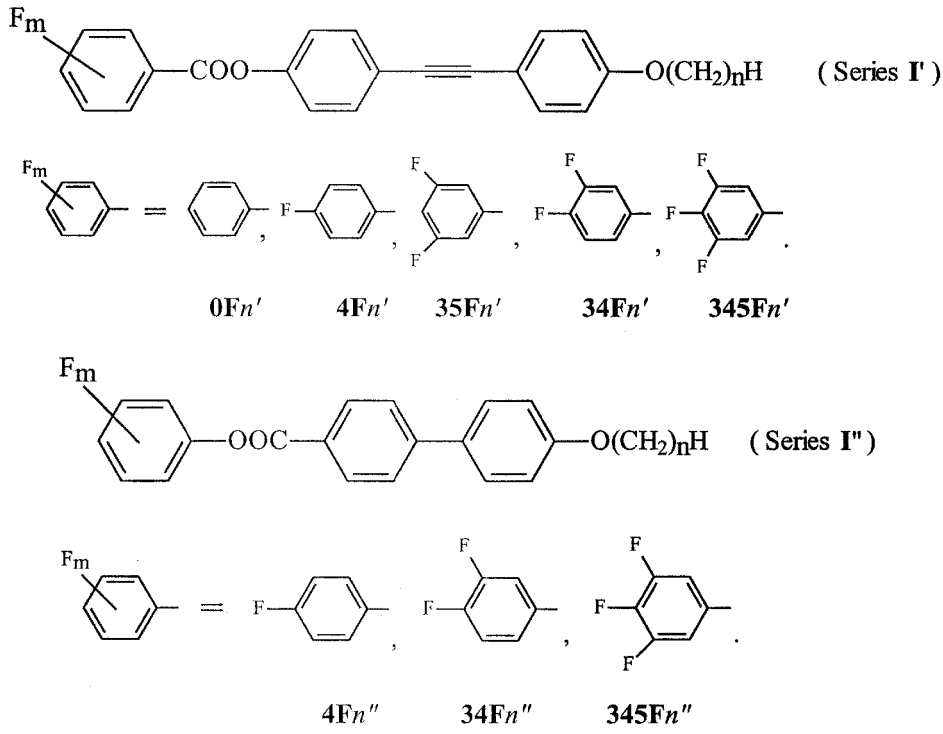


Figure 2. The transition temperatures of several pairs of compounds with opposite ester bond direction.



Scheme 2. The formula of series **I′** and **I″** compounds.

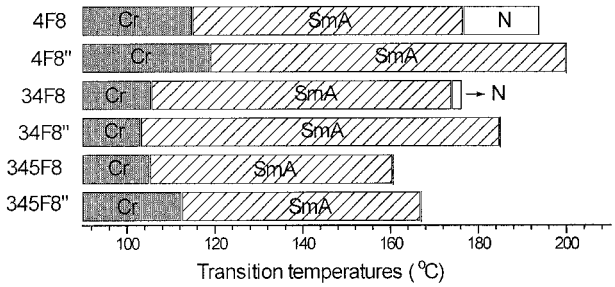


Figure 3. The effect of triple bond on transition temperatures.

show mesophases more stable than those of compounds **I′** in the series with the *para*-fluoro substituent; in the series without the *para*-fluoro substituent the stability order is reversed. For smectic phase formation, lateral attractions are essential. The compounds of series **I″** have conjugation between the alkoxy and the carboxy groups; this should increase the polarity of the carbonyl oxygen, thus leading to an increased intermolecular dipole–dipole interaction. The series **I″** compounds therefore tend to form smectic phases preferently to the corresponding compounds in series **I′**.

In addition, the mesophases stability of series **I″** is greater than that of series **I′**. This may be because the latter's triple bond weakens conjugation between the alkoxy and carboxy groups. It may be for the same reason that series **I″** compounds tend to form smectic phases more readily than the corresponding series **I′** compounds.

In conclusion, the phenomenon of smectic phases being enhanced not only by *meta*-fluoro substitution but also by *para*-fluoro substitution on the terminal phenyl group has been found in many homologous series. The direction of the ester bonds and the existence of triple bonds also affect the mesomorphic properties of these compounds.

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