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Synthesis and mesomorphic properties of several series of fluorinated ester liquid crystals

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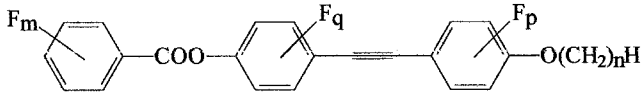
Eight series of fluorosubstituted three-ring ester liquid crystals have been synthesized. Polarizing microscopic textural observations and DSC measurements of their phase transitions show that most are thermotropic liquid crystals with nematic and smectic A phases; furthermore, several show monotropic high order smectic phases. The results showed that the SmA phase is enhanced with the increasing number of fluoro-substituents at the *para*- and *meta*-positions of the terminal phenyl groups. The mesomorphic properties of these compounds are also affected by the direction of the ester bonds. The effect of the triple bond is also discussed.

1. Introduction

Fluorinated liquid crystals have for many years been a focus of research in the liquid crystal field. Many patents have been published on systems with fluoro substituents in the terminal phenyl ring, and this type of liquid crystal has been widely used in nematic mixtures for TFT applications. In addition, the effect of lateral fluoro substitution in liquid crystals is well reported and summarized [1–12]. It is found that such a small substituent may be acceptable in a lateral position without significantly increasing the viscosities; the effect on T_c values depends on whether the increased molecular polarizability or broadening of the molecules is dominant [2]. But the phenomena of enhanced SmA phase formation from both *para*- and *meta*-fluoro substitution on the terminal phenyl group, in the series shown below, is not well studied [13–15].



m = 1, 2, 3; q = 0, 2; p = 0, 2, 4.

To study this phenomenon further, as well as the effect of the direction of the ester bond, the effect of *para*-, *meta*- and *ortho*-fluoro substitution and the effect of the triple bond, eight series of compounds were synthesized by changing the number and position of fluoro substituents and the ester bond direction of these compounds.

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2. Experimental

2.1. *Characterization*

Infrared spectra were obtained on a PE-983G spectrophotometer. ^{1}H NMR spectra, with TMS as internal NMR standard, were recorded on a Varian EM 360L spectrometer, Fx-90Q (90 MHz); ^{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. Mass spectra were measured with a Finnigan 4021 spectrometer. Elemental analyses were performed on a Heraeus (Germany) Rapid CHN-O instrument. The mesophase textures were observed on an Olympus BH2 polarizing microscope in conjunction with a Mettler FP-52 hot stage equipped with an FP-5 control unit. The transition temperatures were confirmed by differential scanning calorimetry (DSC) at a heating rate of 5°C min^{-1} and cooling naturally in a nitrogen atmosphere on a Shimadzu DSC-50 system and data station; the transition peaks were taken as the transition temperatures.

2.2. *Synthesis*

The synthesis of the target molecules is outlined in scheme 1.

Compound **5** and other fluorinated phenols can be easily obtained according to published procedures [16]. The 4-*n*-alkoxybiphenyl-4′-carboxylic acids were prepared in four steps using a slight modification of the procedure reported by Gray *et al.* [17, 18]. Finally compounds **2F***n*, **24***n*, **34***n*, **345***n* and **26***n* were obtained by esterification between the appropriate fluorinated phenol

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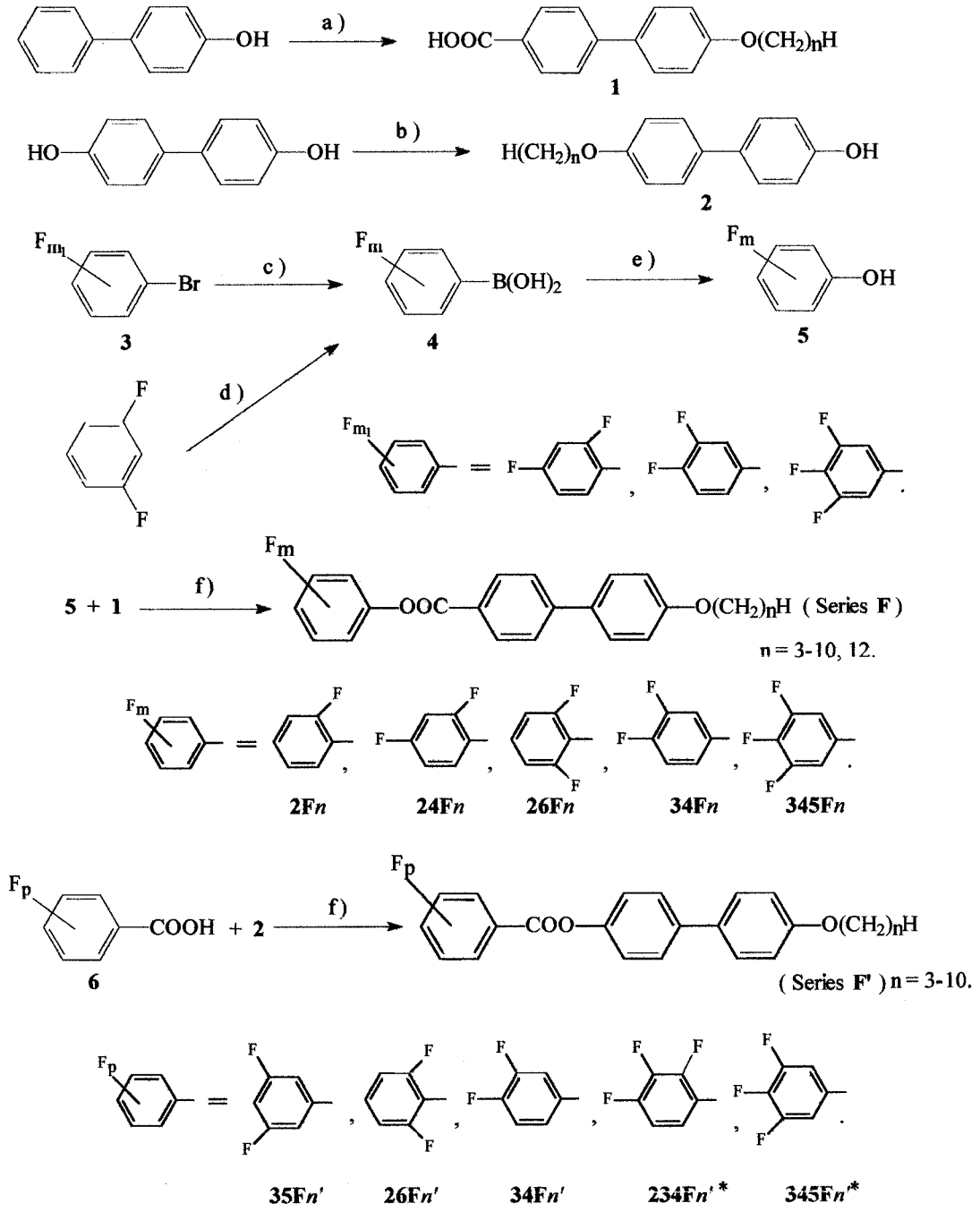


Scheme 1. Synthesis route. Reagents and condition: (a) (1) CH_3COCl, CS_2, $AlCl_3$, reflux; (2) NaBrO, dioxane/water r.t.; (b) NaH; *n*-$C_nH_{2n+1}Br$, DMF, 110°C; (c) (1) Mg, $C_2H_5OC_2H_5$, −78°C; (2) $B(OCH_3)_3$, −78°C to r.t.; (3) HCl/H_2O; (f) H_2O_2, r.t.; (d) (1) LiC_4H_9-*n*, −78°C; (2) $B(OCH_3)_3$, −78°C to r.t.; (3) HCl/H_2O; (e) (1) H_2O_2, (2) HCl/H_2O; (f) DCC/DMAP, THF, r.t. *Compounds **234F***n*′ and **345F***n*′ have been reported previously [19].

and acid using the DCC/DMAP system. Fluorinated benzoic acids and compounds **34F***n*′, **35F***n*′ and **26F***n*′ could also be obtained through the same reaction system by literature methods.

All the compounds of series **F** were prepared by esterification of the corresponding phenol with acid **5**. A typical example of this procedure for synthesis of **2F**9 is given below. Characterization data are given for other representative series members. All of the final 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. All of the target compounds gave satisfactory ^{1}H and ^{19}F NMR, IR, EA and MS spectra data.

2.2.1. *2-Fluorophenyl 4′-n-nonoxybiphenyl-4-carboxylate (**2F**9)*

4-*n*-Nonoxybiphenyl-4′-carboxylic acid (200 mg, 0.59 mmol), 2-fluorophenol (69 mg, 0.49 mmol), *N*,*N*′-dicyclohexylcarbodiimide (125 mg, 0.61 mmol), catalytic DMAP and dry THF (10 ml) were stirred under N_2 at room temperature for 48 h. The mixture was filtered and the residue washed with THF. The collected filtrates were evaporated on a rotary evaporator. The residue was purified by flash chromatography and recrystallized from acetone/methanol to give 173 mg of white solid (**2F**9); yield 67.6%. IR (KBr) ν_{max}: 2927, 1751, 1602, 1505, 1261, 1188, 1078, 832, 751 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.87–0.91 (m, 3H), 1.11–1.99 (m, 14H), 3.99–4.04 (t, 2H, $J = 6.5$ Hz), 6.99–8.27 (m, 12H). ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 51.0 (s, 1F). MS *m*/*z* (rel. int.): 323 (100.00), 435 ($M^+ + 1$, 2.67). Anal. for $C_{28}H_{31}FO_3$: calcd, C 77.39, H 7.19, F 4.37; found, C 77.65, H 7.39 F 4.07%.

2.2.2. *2,4-Difluorophenyl 4′-n-nonoxybiphenyl-4-carboxylate (**24F**9)*

IR (KBr) ν_{max}: 2900, 1740, 1600, 1520, 1300, 1280, 1200, 1150, 1080, 960, 840, 760, 690 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.97–1.26 (m, 3H), 1.40–2.50 (m, 14H), 4.13–4.35 (t, 2H, $J = 6.5$ Hz), 7.00–8.57 (m, 11H). ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 34.6 (s, 1F) 45.3 (s, 1F). MS *m*/*z* (rel. int.): 323 (100.00), 452 (M^+, 1.37). Anal. for $C_{28}H_{30}F_2O_3$: calcd, C 74.32, H 6.68, F 8.40; found, C 74.06, H 6.52 F 8.39%.

2.2.3. *3,4-Difluorophenyl 4′-n-nonoxybiphenyl-4-carboxylate (**34F**9)*

IR (KBr) ν_{max}: 2918, 2850, 1725, 1602, 1520, 1254, 1156 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.89 (t, 3H, CH_3), 1.32–1.88 (m, 14H, $7\times CH_2$), 4.00 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.90–7.10 (m, 5H, ArH), 7.49–7.67 (m, 4H, ArH), 8.12 (d, $J = 9$ Hz, 2H, ArH). ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 56.89 (m, F), 73.40 (m, F). MS *m*/*z* (rel. int.): 452 (M^+, 2.44), 323 ($C_9H_{19}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 27.05). Anal. for $C_{28}H_{30}F_2O_3$: calcd, C 74.32, H 6.68, F 8.40; found C 74.26, H 6.70, F 8.34%.

2.2.4. *2,6-Difluorophenyl 4′-n-heptoxybiphenyl-4-carboxylate (**26F**7)*

IR (KBr) ν_{max}: 2933, 2854, 1743, 1605, 1498, 1265, 1188 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.92 (t, 3H, CH_3), 1.40–1.89 (m, 10H, $5\times CH_2$), 4.00 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.90–7.13 (m, 5H, ArH), 7.57–7.77 (m, 4H, ArH), 8.28 (d, $J = 9$ Hz, 2H, ArH). ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 48.90 (s, F). MS *m*/*z* (rel. int.): 424 (M^+, 1.85), 295 ($C_7H_{15}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 10.88). Anal. for $C_{26}H_{26}F_2O_3$: calcd, C 73.57, H 6.17, F 8.95; found C 73.51, H 6.30, F 8.82%.

2.2.5. *3,4,5-Trifluorophenyl 4′-n-nonoxybiphenyl-4-carboxylate (**345F**9)*

IR (KBr) ν_{max}: 2925, 2855, 1740, 1601, 1527, 1242, 1201 cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.40–1.92 (m, 4H, $2\times CH_2$), 4.01 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.87–7.05 (m, 4H, ArH), 7.54–7.74 (m, 4H, ArH), 8.19 (d, $J = 6.0$ Hz, 2H, ArH). ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 55.14 (m, 2F), 86.11 (m, F). MS *m*/*z* (rel. int.): 470 (M^+, 4.90), 323 ($C_9H_{19}OC_6H_4$–$C_6H_4CO^+$, 100.00), 197 (HOC_6H_4–$C_6H_4CO^+$, 30.68). Anal. for $C_{28}H_{29}F_3O_3$: calcd, C 71.47, H 6.21, F 12.11; found C 71.47, H 6.19, F 12.02%.

2.2.6. *4′-n-Nonoxybiphenyl-4-ol 3,4-difluorobenzoate (**34F**9′)*

IR (KBr) ν_{max}: 2920, 2852 (s, C–H), 1734 (vs, C=O), 1608 (s, C_6H_4), 1519 (vs, $C_6H_3F_2$), 1257, 1171 (s, C–O–C) cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.32–1.76 (m, 14H, $7\times CH_2$), 3.95 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.95 (d, 2H, ArH), 7.18–7.28 (m, 3H, ArH), 7.43–7.63 (m, 4H, ArH), 7.93–8.13 (m, 2H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 52.85 (m, F), 60.02 (m, F) ppm. MS *m*/*z* (rel. int.): 452 (M^+, 65.78), 326 ($C_6H_3F_2COOC_6H_4C_6H_4OH^+$, 18.24), 141 ($C_6H_3F_2CO^+$, 100.00). Anal. for $C_{28}H_{30}F_2O_3$: calcd. C 74.32, H 6.68, F 8.40; found, C 74.52, H 6.77, F 8.27%.

2.2.7. *4′-n-Nonoxybiphenyl-4-ol 3,5-difluorobenzoate (**35F**9′)*

IR (KBr) ν_{max}: 2920, 2852 (s, C–H), 1740 (vs, C=O), 1596 (s, C_6H_4), 1496 (vs, $C_6H_3F_2$), 1271, 1171 (s, C–O–C) cm^{-1}. ^{1}H NMR δ_H (90 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.32–1.90 (m, 14H, $7\times CH_2$), 3.99 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.87–7.23 (m, 5H, ArH), 7.40–7.77 (m, 6H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 31.11 (s, F) ppm. MS *m*/*z* (rel. int.): 452 (M^+, 68.03), 326 ($C_6H_3F_2$–COO–$C_6H_4C_6H_4OH^+$, 48.45), 141 ($C_6H_3F_2CO^+$, 100.00). Anal. for $C_{28}H_{30}F_2O_3$: calcd. C 74.32, H 6.68, F 8.40; found, C 74.55, H 6.65, F 8.45%.

2.2.8. *4′-n-Nonoxybiphenyl-4-ol 2,6-difluorobenzoate (**26F**9′)*

IR (KBr) ν_{max}: 2921, 2852 (s, C–H), 1748 (vs, C=O), 1606, 1495 (vs, ArH), 1271, 1172 (s, C–O–C) cm^{-1}. ^1H NMR δ_H (60 MHz; $CDCl_3$; TMS): 0.90 (t, 3H, CH_3), 1.30–1.95 (m, 14H, $7 \times CH_2$), 4.05 (t, $J = 6.0$ Hz, 2H, RCH_2O), 6.95–7.75 (m, 11H, ArH) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 42.89 (s, F) ppm. MS *m/z* (rel. int.): 452 (M^+, 32.67), 326 ($C_6H_3F_2$–COO–$C_6H_4C_6H_4OH^+$, 9.25), 141 ($C_6H_3F_2CO^+$, 100.00). Anal. for $C_{28}H_{30}F_2O_3$: calcd. C 74.32, H 6.68, F 8.40; found, C 74.35, H 6.64, F 8.38%.

3. Results and discussion

The phase transition temperatures of all the compounds were determined by DSC; the mesomorphic textures were observed by polarizing optical microscopy to determine the types of mesophases. The transition temperatures shown in tables 1 and 2 were the maxima of transition peaks on each DSC trace. The clearing points of the compounds synthesized are plotted against the number of carbon atoms in the alkoxy chain, *n*, in figures 1, and 2.

All compounds are liquid crystals except **2F**3. Most series **F** compounds showed enantiotropic SmA and/or N phases. With increasing hydrocarbon chain length, clearing points gradually drop. Compounds **34F***n* and **345F***n* show only enantiotropic SmA phases. Most of compounds **24F***n* and **2F***n* show both nematic and SmA phases. Compounds **26F**5 and **26F**7 show enantiotropic N and monotropic SmA phases.

To study the effect of *para*-fluoro substitution, compounds **24F***n* and **2F***n* were studied. With the introduction of the *para*-fluoro substituent, the T_c and $T_{SmA\text{-}N}$ were both increased, as was the width of SmA phase range, but the nematic phase range decreased. Compound **2F**3 was not liquid crystalline, but because of the increase in the length/diameter ratio, **24F**3 was a nematic liquid crystal.

Table 1. The phase transition temperatures of series **2F***n*, **24F***n*, **34F***n*, **345F***n* and **26F***n*. Cr = crystal; N = nematic; SmA = smectic A; I = isotropic; Recr = recrystal.

Compound	*n*	Phase transition temperatures/°C
2F3	3	Cr 142.3 I 122.4 Recr
2F5	5	Cr 89.2 SmA 112.2 N 123.7 I 121.9 N 110.4 SmA 57.2 Recr
2F6	6	Cr 86.4 SmA 109.8 N 121.0 I 118.6 N 107.0 SmA 38.5 Recr
2F7	7	Cr 71.4 SmA 111.3 N 119.7 I 118.5 N 109.7 SmA 44.4 Recr
2F8	8	Cr 80.1 SmA 115.0 N 122.2 I 120.6 N 113.7 SmA 20.8 Recr
2F9	9	Cr 82.2 SmA 112.3 N 117.0 I 115.0 N 110.3 SmA 43.5 Recr
2F10	10	Cr 81.8 SmA 114.0 N 117.9 I 116.7 N 112.6 SmA 31.7 Recr
2F12	12	Cr 75.0 SmA 114.3 N 115.2 I 113.0 N 111.8 SmA 47.2 Recr
24F3	3	Cr 138.2 N 187.2 I 185.8 N 103.3 Recr
24F6	6	Cr 84.2 SmA 150.9 N 169.6 I 168.3 N 149.3 SmA 76.1 Recr
24F7	7	Cr 85.5 SmA 153.2 N 163.8 I 162.5 N 151.7 SmA 68.2 Recr
24F8	8	Cr 83.9 SmA 154.4 N 162.1 I 160.9 N 152.7 SmA 72.9 Recr
24F9	9	Cr 90.9 SmA 153.3 N 156.6 I 155.1 N 151.7 SmA 64.1 Recr
24F10	10	Cr 90.1 SmA 154.3 N 156.1 I 154.8 N 152.9 SmA 66.7 Recr
24F12	12	Cr 93.6 SmA 151.4 I 149.9 SmA 73.4 Recr
34F4	4	Cr 129.8 SmA 192.5 I 190.9 SmA 106.6 Recr
34F5	5	Cr 126.8 SmA 189.9 I 188.2 SmA 105.3 Recr
34F6	6	Cr 116.1 SmA 190.4 I 188.0 SmA 89.5 Recr
34F7	7	Cr 102.1 SmA 187.0 I 185.3 SmA 85.8 Recr
34F8	8	Cr 103.3 SmA 185.0 I 183.2 SmA 86.7 Recr
34F9	9	Cr 98.8 SmA 183.0 I 180.9 SmA 77.2 Recr
34F10	10	Cr 101.6 SmA 180.9 I 179.0 SmA 79.4 Recr
345F4	4	Cr 129.4 SmA 170.9 I 168.8 SmA 112.6 Recr
345F5	5	Cr 128.8 SmA 169.0 I 167.2 SmA 108.5 Recr
345F6	6	Cr 119.3 Sma 168.1 I 166.4 SmA 103.5 Recr
345F7	7	Cr 118.6 SmA 168.3 I 166.2 SmA 97.2 Recr
345F8	8	Cr 112.6 SmA 167.0 I 164.8 SmA 91.9 Recr
345F9	9	Cr 115.5 Sma 165.1 I 163.0 SmA 91.4 Recr
345F10	10	Cr 111.7 SmA 163.0 I 160.6 SmA 85.9 Recr
26F4	4	Cr 114.4 I 107.7 N 98.4 SmA 83.3 Recr
26F5	5	Cr 86.7 N 98.1 I 96.7 N 84.2 SmA 58.8 Recr
26F7	7	Cr 85.5 N 94.7 I 93.6 N 79.7 SmA 33.9 Recr

Table 2. The mesomorphic properties of compounds **34F***n*′, **35F***n*′ and **26F***n*′. Cr = crystal; CrE = crystal E; SmA = smectic A; SmB = smectic B; N = nematic; I = isotropic; Recr = recrystal.

Compound	*n*	Phase transition temperatures/°C
34F4′	4	Cr 121.1 CrE 127.2 SmA 194.1 N 195.1 I 193.5 N 192.5 SmA 125.4 CrE 111.3 Recr
34F5′	5	Cr 107.8 SmB 113.7 SmA 191.1 I 189.5 SmA 112.6 SmB 104.1 Recr
34F6′	6	Cr 108.8 SmB 112.0 SmA 189.9 I 188.1 SmA 111.7 SmB 102.2 CrE 100.5 Recr
34F7′	7	Cr 103.0 SmB 110.2 SmA 187.7 I 185.7 SmA 108.5 SmB 90.3 CrE 83.3 Recr
34F8′	8	Cr 108.6 SmA 188.5 I 186.3 SmA 110.7 SmB 87.0 CrE 76.1 Recr
34F9′	9	Cr 107.2 SmA 182.4 I 179.2 SmA 107.6 SmB 82.2 Recr
34F10′	10	Cr 108.0 SmA 181.9 I 179.0 SmA 107.7 SmB 89.1 Recr
35F4′	4	Cr 129.7 CrE 150.3 SmA 176.0 I 174.0 SmA 148.6 CrE 99.0 Recr
35F5′	5	Cr 110.7 CrE 128.2 SmA 166.1 I 164.0 SmA 126.4 CrE 101.9 Recr
35F6′	6	Cr 100.2 CrE 134.6 SmA 165.8 I 163.4 SmA 132.4 CrE 89.7 Recr
35F7′	7	Cr 114.6 SmA 160.2 I 158.1 SmA 112.2 CrE 109.2 Recr
35F8′	8	Cr 111.2 SmA 157.8 I 155.5 SmA 107.5 SmB 104.4 Recr
35F9′	9	Cr 111.1 SmA 152.2 I 150.4 SmA 97.3 SmB 92.2 Recr
35F10′	10	Cr 111.7 SmA 150.3 I 148.7 SmA 95.5 Recr
26F4′	4	Cr 105.7 I 84.2 N 74.1 Recr
26F5′	5	Cr 92.8 I 69.9 N 63.2 Recr
26F6′	6	Cr 96.3 I 80.5 N 71.0 Recr
26F7′	7	Cr 90.9 I 74.7 N 73.5 Recr
26F8′	8	Cr 88.2 I 82.3 N 76.4 Recr
26F9′	9	Cr 81.2 I 79.6 N 73.2 Recr
26F10′	10	Cr 85.0 I 83.2 N 77.5 Recr

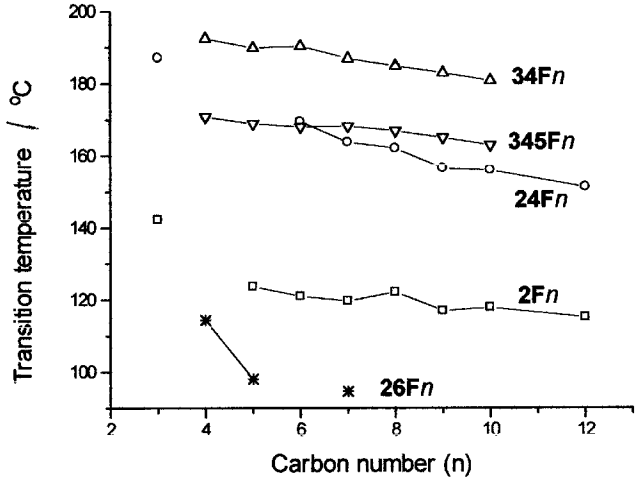


Figure 1. Clearing points as a function of the number of carbon atoms in the alkoxy chain for series **2F***n*, **24F***n*, **245F***n*, **34F***n* and **26F***n*.

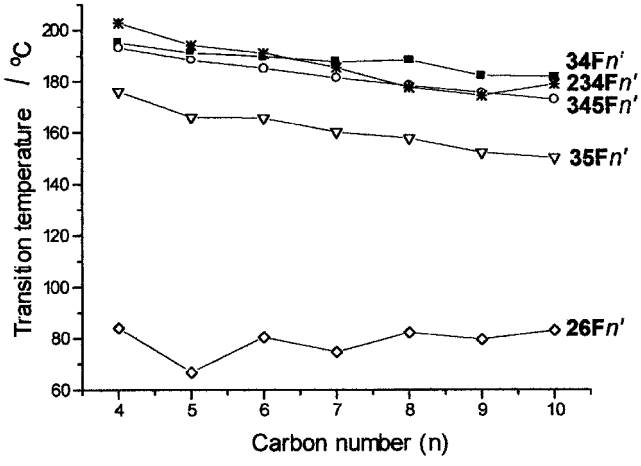
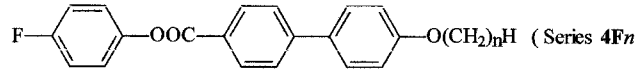


Figure 2. Clearing points (or $T_{I\text{-}N}$ of compounds **26F***n*′) as a function the number of carbon atoms in the alkoxy chain for compounds **34F***n*′, **234F***n*′, **345F***n*′, **35Fn**′ and **26F***n*′.

The effect of *meta*-fluoro substitution could be found from compounds **4F**8 [20], **34F**8 and **345F**8. With the introduction of the *meta*-fluoro substituent, the T_c decreased, the SmB phase disappeared and only SmA phases were found in compounds **34F***n* and **345F***n*.

From the mesomorphic properties of compounds **26F***n* and **2F***n*, the *ortho*-fluoro substitution was studied. Because of the interaction between the fluorine atom and the oxygen atom of the carbonyl group, the *ortho*-fluoro substituent increases not only the width but also the thickness of the molecule. This causes the clearing points to decrease sharply, and enantiotropic SmA phases to become monotropic.



4F*8* Cr119 SmA 200 I 200 SmA 110 SmB 70 Recr (°C)

Turning to series **F**′, compounds **34F***n*′ and **35F***n*′ show enantiotropic N, SmA, enantiotropic/monotropic

CrE and SmB phases. Compounds **26F***n*′ show only monotropic N phases. The *para*-, *meta*- and *ortho*-fluoro substitutions show almost the same effects as in series **F** (see table 2 and figure 2). Moreover, the difference between the mesomorphic properties of compounds **234F***n*′ and compounds **34F***n*′ should be noted. The introduction of the *ortho*-fluoro substituent increased the clearing points when $n \leqslant 6$, and decreased them when $n \geqslant 7$. This might be because, on the one hand, *ortho*-fluoro substitution enhanced the polarity and polarizability of the molecule; or on the other hand, because the interaction between the fluorine atom and oxygen atom of the carboxy group thickened the molecule. Compound **34F**4′ showed enantiotropic N and SmA phases. With the introduction of a *meta*-fluoro substituent in compound **345F**4′, only an enantiotropic SmA phase was found. From the mesomorphic properties of these two compounds, it is again seen that *meta*-fluoro substitution on the terminal phenyl group enhances the formation of the SmA phase [13–15].

Because of its large electronegativity and small size, the fluoro substituent yields much negative charge. With the increase from two fluoro substituents to three on the terminal phenyl group, the distances between terminal groups were increased. The terminal–terminal attractions were weakened, and smectic phase formation enhanced.

The effect of an introduced triple bond was also studied (see scheme 2 and figures 3 and 4). On the introduction of the triple bond, monotropic liquid crystal **26F**8′ change to enantiotropic **26F**8″ because of the increase of the length/diameter ratio. For some structures, the clearing points decreased, and nematic phases formation was enhanced. Possibly the triple bond interfered with the conjugation of the whole molecule; the lateral–lateral interactions were then weakened.

From figure 5 the effect of the direction of ester bond can be studied. In the series without the *para*-fluoro

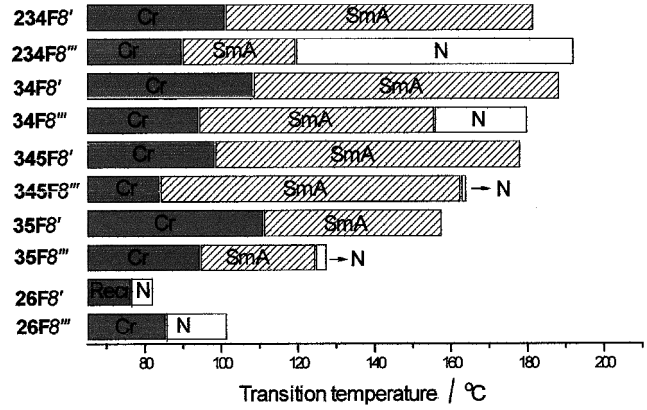
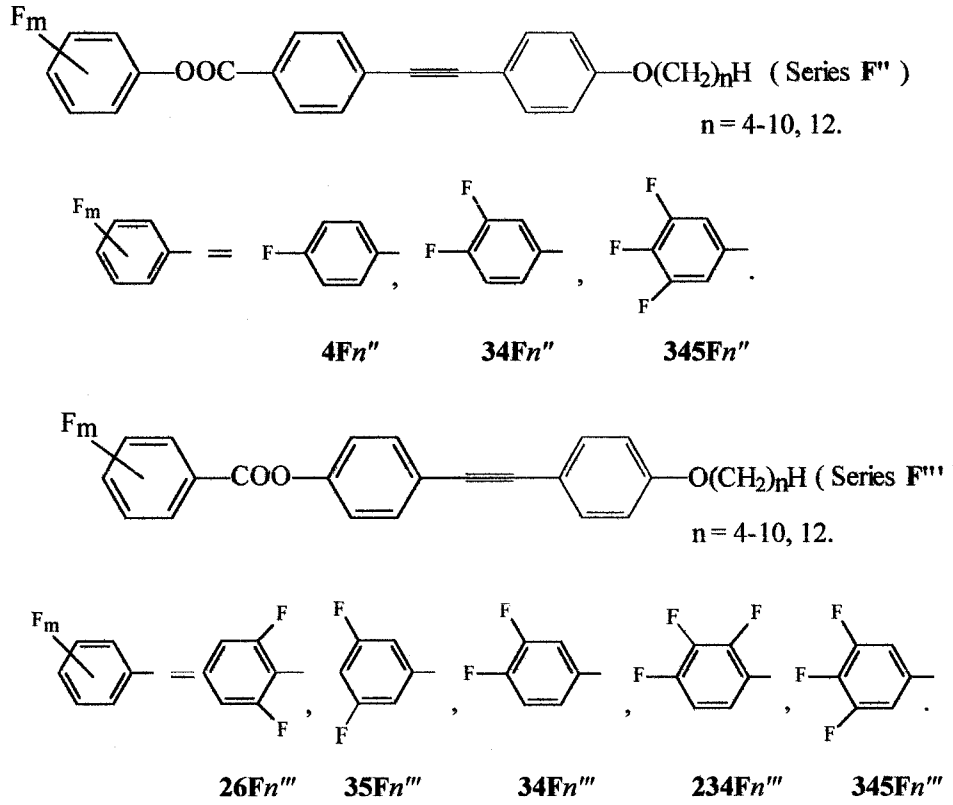


Figure 3. The effect of a triple bond on mesomorphic properties.



Scheme 2. The molecular structures of series **F**″ and **F**‴.

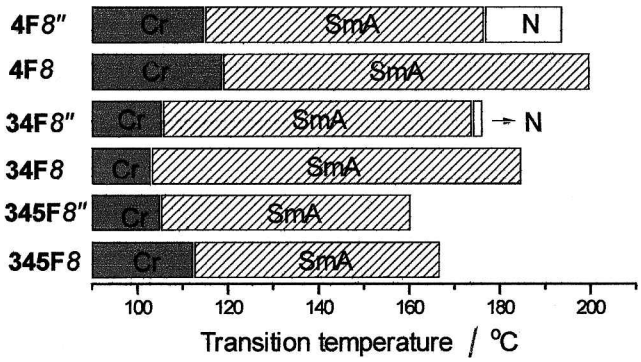


Figure 4. The effect of triple bond on the mesomorphic properties.

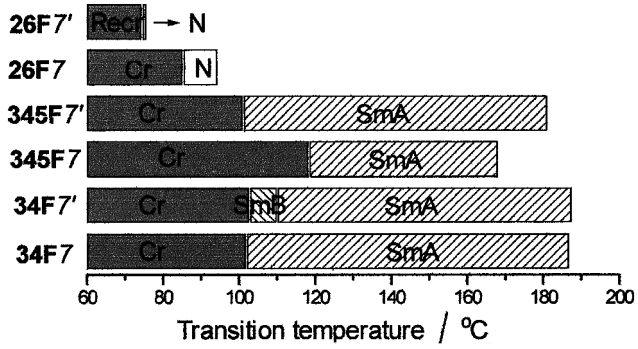


Figure 5. The effect of ester bond direction.

substituent, enantiotropic N and monotropic SmA phases were found in compound **26F**7, but only a monotropic N phase was found in compound **26F**7′; for smectic phase formation, lateral attractions are essential. Compound **26F**7 has conjugation between the alkoxy and the carbonyl groups; this should increase the polarity of the carbonyl oxygen, leading to increased intermolecular dipole–dipole interaction. Also, compound **26F**7 has a greater tendency to form smectic phases than the corresponding compound **26F**7′. Turning to compounds with the *para*-fluoro substituent the clearing points of compounds **34F**7′ and **345F**7′ are higher than those of the corresponding **34F**7 and **345F**7. This is similar to the fact that the clearing points of compounds **34F**8‴ and **345F**8‴ are higher than those of the corresponding **34F**8″ and **345F**8″ (see figures 3 and 4).

In conclusion it may be noted that (i) the SmA phase is enhanced with the increasing number of fluoro substituents at the *para*- and *meta*-positions of the terminal phenyl groups; (ii) the direction of the ester bond controls the polarity of the molecule, which affects its mesomorphic properties; (iii) the introduction of a triple bond usually enhances the ability to form liquid crystalline phases, but sometimes decreases the $T_{N\text{-}I}$ or $T_{SmA\text{-}I}$.

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