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Synthesis and mesomorphic properties of chiral fluorinated liquid crystals

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Some fluorinated chiral liquid crystals were synthesized and the compounds characterized by IR, ^{1}H NMR, ^{19}F NMR and mass spectroscopy and elemental analysis. Their phase transition behaviour was investigated by differential scanning calorimetry and polarizing optical microscopy. Nearly all of the compounds synthesized are liquid crystals with an enantiotropic cholesteric phase. Some of them exhibit a blue phase. Lateral tetrafluoro substitution decreases the clearing point and molecular polarity affects the formation of liquid crystalline phases.

1. Introduction

Fluorinated liquid crystals are highly resistant to light and heat. In particular, these materials exhibit the fast voltage–time responses that are required in TFT liquid crystal displays (LCDs). Generally, fluorinated liquid crystals (LCs) have low viscosity, which can improve the response speed of an LCD. Therefore, many kinds of fluorinated LC have been designed and synthesized [1–4]. In previous studies, several series of LCs with 1,4-tetrafluorophenylene groups were synthesized [5–8]. Generally, the tetrafluoro substitution strongly enhances the formation of a nematic phase. Hence, they have potential for use in LCD mixtures.

Chiral smectic LCs are one of the most interesting systems for display devices, especially LCs that exhibit chiral smectic C (SmC*) or chiral antiferroelectric smectic C (SmC_A*) phases [9]. Two series of chiral LCs with 1,4-tetrafluorophenylene groups have been synthesized [10, 11]. Some of them exhibit a monotropic SmC* phase, which is of potential use in ferroelectric LCD mixtures. To search for new LCs for LCDs and study the relationship between molecular structure and liquid crystalline properties, two other series of chiral LCs with 1,4-tetrafluorophenylene groups were synthesized.

2. Characterization

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

The phase transition temperatures of the target compounds were measured by polarizing optical microscopy (POM, Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (DSC, Shimidazu 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. Phase identification was made by comparing the observed textures with those reported in the literature.

3. Synthesis

The compounds were obtained by routes depicted in schemes 1–2. The intermediates and final compounds were synthesized according to literature methods [8, 12, 13].

3.1. *Compound I8*

A typical synthetic procedure is as follows. To a mixture of 4-octyloxytetrafluorophenylacetylene (0.43 mmol), compound **1** (0.39 mmol), bis(triphenylphosphine)palladium dichloride (20 mg), triphenylphosphine (60 mg)

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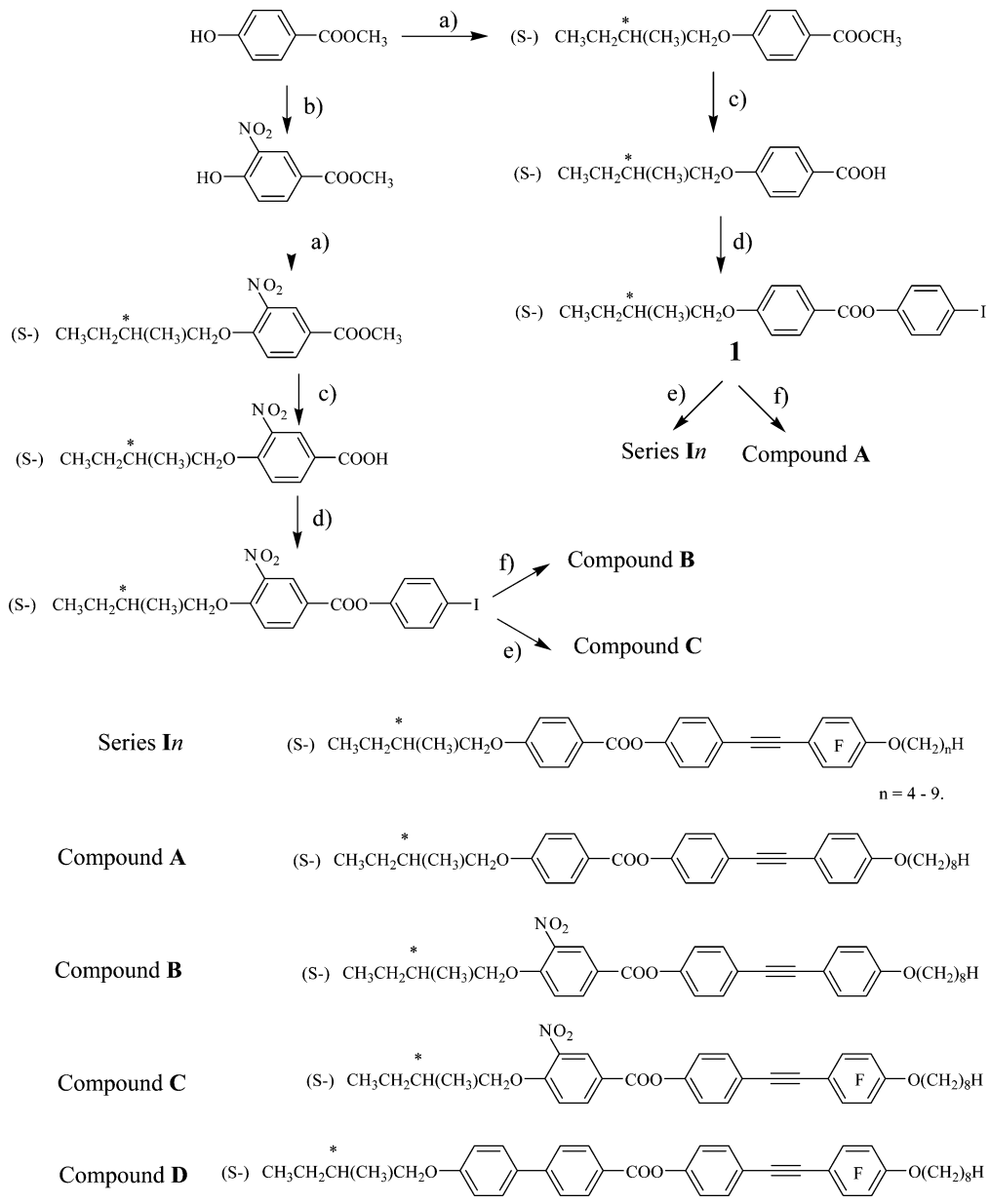
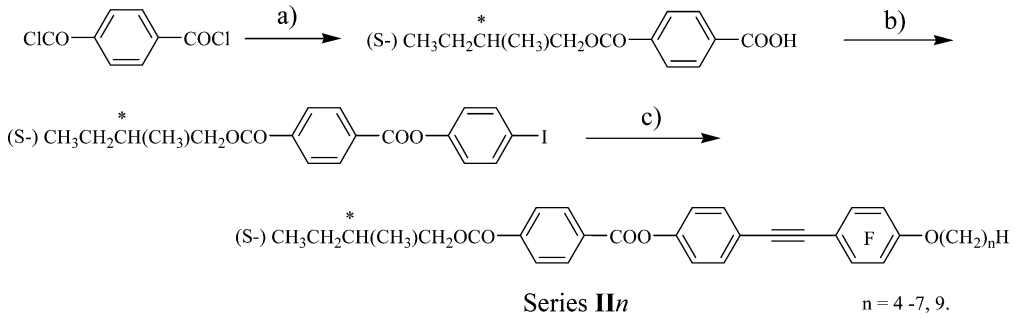


Scheme 1. Synthesis of compounds **I*n***, **A**, **B**, and **C**, as well as the molecular structure of compound **D**. (a) (*S*)-$C_2H_5C^*H(CH_3)CH_2OH$, DEAD/PPh_3, THF; (b) HNO_3; (c) (1) NaOH aq., EtOH (2) HCl aq.; (d) *p*-iodophenol/DCC/DMAP, THF; (e) 4-alkoxytetrafluorophenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N; (f) 4-octyloxyphenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N.

and CuI (60 mg) under dry N_2, was added 20 ml of anhydrous triethylamine. The mixture obtained was heated under reflux under stirring for 2 h. Analysis by thin-layer chromatography (TLC) revealed completion of the reaction. The precipitate formed was then filtered off and washed with ether. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane as eluent. The obtained compound was recrystallized from acetone/methanol. $[\alpha]_D^{20} = +5.40$ (25°C, $CHCl_3$). M.p. 70.6°C. IR (KBr, cm^{-1}): 2925, 2854, 2217, 1729, 1605, 1513, 1490, 1203, 1171, 846. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ (ppm) 0.91–1.94 (m, 24H, aliphatic hydrogens), 3.82–3.91 (dd, 2H, RCH_2O), 4.27 (t, J=6 Hz, 2H, RCH_2O), 6.96 (d, J=9 Hz, 2H, ArH), 7.22 (d, J=7.5 Hz, 2H, ArH), 7.61 (d, J=7.5 Hz, 2H, ArH), 8.12 (d, J=9 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA): δ (ppm) 61.10 (d, J=18.8 Hz, 2F), 80.20 (d, J=18.8 Hz, 2F). MS m/z (rel. int.): 584 (M^+, 0.35), 191 ($C_5H_{11}OC_6H_4CO^+$, 100.00), 121



Scheme 2. Synthesis of compounds **II*n***. (a) (1) (S-) $C_2H_5C^*H(CH_3)CH_2OH$; (2) HCl aq.; (b) *p*-iodophenol/DCC/DMAP, THF; (c) 4-alkoxytetrafluorophenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, THF/Et_3N.

($HOC_6H_4CO^+$, 86.27). Elemental analysis: calculated for $C_{34}H_{36}F_4O_4$, C 69.85, H 6.21, F 13.00%; found, C 69.82, H 6.17, F 13.03%.

3.2. *Compound A*

$[\alpha]_D^{20}$= +4.05 (25°C, $CHCl_3$). M.p. 112.0°C. IR (KBr, cm^{-1}): 2924, 2854, 2217, 1729, 1604, 1511, 1467, 1208, 1165, 836. ^1H NMR (60 MHz, $CDCl_3$, TMS): δ (ppm) 0.84–2.07 (m, 24H, aliphatic hydrogens), 3.79–4.04 (m, 4H), 6.71–7.56 (m, 10H, ArH), 8.07 (d, J = 8 Hz, 2H, ArH). MS m/z (rel. int.): 512 (M^+, 9.21), 191 ($C_5H_{11}OC_6H_4CO^+$, 100.00), 121 ($HOC_6H_4CO^+$, 71.31). Elemental analysis: calculated for $C_{34}H_{40}O_4$, C 79.65, H 7.86%; found, C 79.64, H 7.98%.

3.3. *Compound B*

$[\alpha]_D^{20}$= +8.86 (25°C, $CHCl_3$). M.p. 102.5°C. IR (KBr, cm^{-1}): 2924, 2854, 2217, 1733, 1623, 1513, 1466, 1202, 1166, 838. ^1H NMR (60 MHz, $CDCl_3$ TMS): δ (ppm) 0.88–2.03 (m, 24H, aliphatic hydrogens), 3.87–4.04 (m, 4H), 4.70 (q, J=6 Hz, H), 6.70–7.60 (m, 9H, ArH), 8.16–8.55 (m, 2H, ArH). MS m/z (rel. int.): 557 (M^+, 10.61), 236 ($C_5H_{11}O(NO_2)C_6H_3CO^+$, 7.51), 166 ($HO(NO_2)C_6H_3CO^+$, 100.00). Elemental analysis: calculated for $C_{34}H_{39}NO_6$, C 73.23, H 7.05, N 2.51%; found, C 72.91, H 7.12, N 2.03%.

3.4. *Compound C*

$[\alpha]_D^{20}$= +5.69 (25°C, $CHCl_3$). M.p. 102.7°C. IR (KBr, cm^{-1}): 2928, 1733, 1623, 1514, 1491, 1204, 1167, 839. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ (ppm) 0.91–1.94 (m, 24H, aliphatic hydrogens), 4.00–4.34 (m, 3H, RCH_2O), 7.11–7.27 (m, 3H, ArH), 7.58–7.67 (m, 2H, ArH), 8.28–8.37 (m, 1H, ArH), 8.66 (s, 1H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA): δ (ppm) 61.10 (d, J=18.8 Hz, 2F), 80.20 (d, J=18.8 Hz, 2F). MS m/z (rel. int.): 630 (M^++1, 0.68), 236 ($C_5H_{11}O(NO_2)C_6H_4CO^+$, 14.60), 166 ($HO(NO_2)C_6H_4CO^+$, 100.00). Elemental analysis: calculated for $C_{34}H_{35}F_4NO_6$, C 64.86, H 5.60, N 2.22, F 12.07%; found, C 64.99, H 5.53, N 2.31, F 12.05%.

3.5. *Compound D*

M.p. 112.0°C. IR (KBr, cm^{-1}): 2923, 1724, 1602, 1491, 1277, 1166, 829. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ (ppm) 0.89–1.93 (m, 26H, aliphatic hydrogens), 3.78–3.87 (m, 2H, RCH_2O), 4.26 (t, J=6.0 Hz, 2H, ArH), 6.94–8.26 (m, 12H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA): δ (ppm) 60.5 (d, J=18.8 Hz, 2F), 79.8 (d, J=18.8 Hz, 2F). MS m/z (rel. int.): 661 (M^++1, 0.67), 267 ($C_5H_{11}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 20.23). Elemental analysis: calculated for $C_{40}H_{40}F_4O_4$, C 72.71, H 6.10, F 11.50%; found, C 72.65, H 6.35, F 11.11%.

3.6. *Compound II7*

IR (KBr, cm^{-1}): 2958, 2221, 1732, 1714, 1491, 1208, 1167, 842. ^1H NMR (90 MHz, $CDCl_3$, TMS): δ (ppm) 0.91–1.94 (m, 22H, aliphatic hydrogens), 4.20–4.36 (m, 4H, RCH_2O), 6.96 (d, J=9 Hz, 2H, ArH), 7.20–8.25 (ArH, 8H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA): δ (ppm) 61.10 (d, J=18.8 Hz, 2F), 80.20 (d, J=18.8 Hz, 2F)ppm. MS m/z (rel. int.): 598 (M^+, 11.62), 219 ($C_5H_{11}OOCC_6H_4CO^+$, 100.00), 149 ($HOOCC_6H_4CO^+$, 34.77). Elemental analysis: calculated for $C_{34}H_{34}F_4O_5$, C 68.22, H 5.72, F 12.69%; found, C 68.20, H 5.74, F 13.07%.

4. Results and discussion

The phase transition temperatures of all the compounds were determined by DSC with a heating rate of 5°C min^{-1}. POM textures were observed to determine the types of mesophases. The transition temperatures presented in both tables are the maxima of the transition peaks on each DSC trace.

The phase transition temperatures of compounds **I*n***, **A**, **B**, **C** and **D** are summarized in table 1. Figure 1 plots the transition temperatures of compounds **I*n*** as a function of the number of methylenic units (*n*) in the alkoxy chain. All of these compounds exhibit an enantiotropic cholesteric phases. The clearing points show a clear odd–even effect.

During the last decade, many LCs with a 1,4-tetrafluorophenylene unit have been synthesized. Generally, the lateral tetrafluoro substitution in the core strongly suppresses the formation of smectic phases and decreases the clearing points. In this study we observed the same phenomena. Figure 2 shows the mesomorphic properties of compounds **I8**, **A**, **B**, **C** and **D**. For the pair of compounds **I8** and **A**, both the clearing and melting points are decreased by lateral tetrafluoro substitution, which strongly decreases the lateral interactions of the molecules. Turning to the pair of compounds **B** and **C**, a similar phenomenon was also found. Compound **B** exhibits an enantiotropic cholesteric phase, but compound **C** exhibits a monotropic cholesteric phase. Turning to the other two pairs of compounds **A/B**, and **I8/A**, although nitro substitution can enhance the nonlinear optical properties of molecules, lateral interactions of molecules are strongly decreased. Therefore, clearing points are decreased and the cholesteric phase ranges become narrow. Comparing compound **D** with **I8**, with the introduction of 1,4-phenylene group, the clearing point increases 128.9°C and an enantiotropic SmA phase is formed. The introduction of 1,4-phenylene group in the core strongly enhances the lateral interactions of molecules.

With the introduction of carboxy groups into compounds **I*n*** between chiral alkoxy and 1,4-phenylene groups, compounds **II*n*** were obtained. Generally, they show enantiotropic cholesteric and blue phases (table 2). The introduction of carboxy groups can increase the symmetry of molecules, but decreases their polarity. This should be the main reason of the formation of blue phase and also the reason that the clearing points of compounds **II*n*** are lower than those of the corresponding compounds **I*n***.

Two of other LC series with 1,4-phenylene groups have been prepared previously [10, 11]. The difference between these two series and the series **I*n*** or **II*n*** reported here is the direction of the ester bond in the cores. Although the previous two series exhibit an enantiotropic or monotropic SmC* phase, series **I*n*** and **II*n*** did not. It

Table 1. Transition temperatures of compounds **I*n***, **A**, **B**, **C** and **D** (Cr=crystal; Ch=cholesteric phase; SmA=smectic A phase; I=isotropic liquid; Recr=recrystallization).

Compound	*n*	Transition temperatures /°C
I4	4	Cr 102.1 Ch 151.7 I 149.8 Ch 69.4 Recr
I5	5	Cr 93.8 Ch 141.1 I 139.9 Ch 53.4 Recr
I6	6	Cr 86.4 Ch 140.1 I 138.7 Ch 45.8 Recr
I7	7	Cr 71.7 Ch 133.2 I 131.9 Ch 42.1 Recr
I8	8	Cr 70.6 Ch 133.2 I 131.3 Ch 34.8 Recr
I9	9	Cr 71.9 Ch 127.2 I 125.8 Ch 45.4 Recr
A		Cr 112.0 Ch 183.6 I 181.5 Ch 96.0 Recr
B		Cr 102.5 Ch 143.4 I 142.0 Ch 79.5 Recr
C		Cr 102.7 I 96.5 Ch 67.5 Recr
D		Cr 112.0 SmA 206.8 Ch 262.1 I 260.4 Ch 204.0 SmA 86.7 Recr

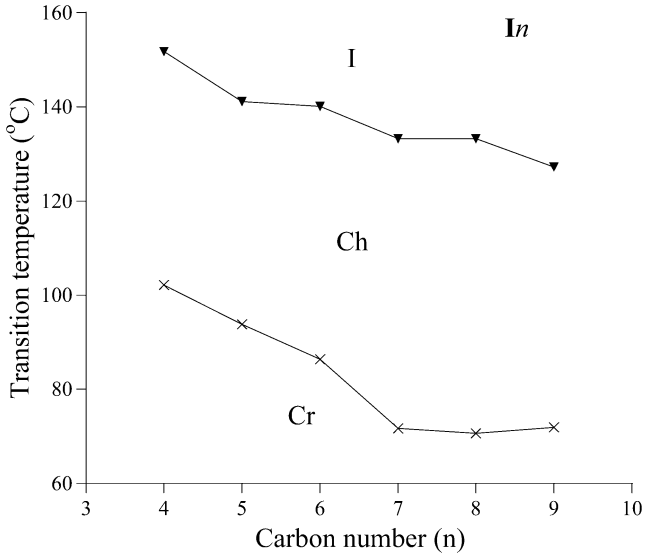


Figure 1. Transition behaviour of the compounds **I*n***: dependence of the transition temperatures on the number (*n*) of methylene units of the alkoxy chain.

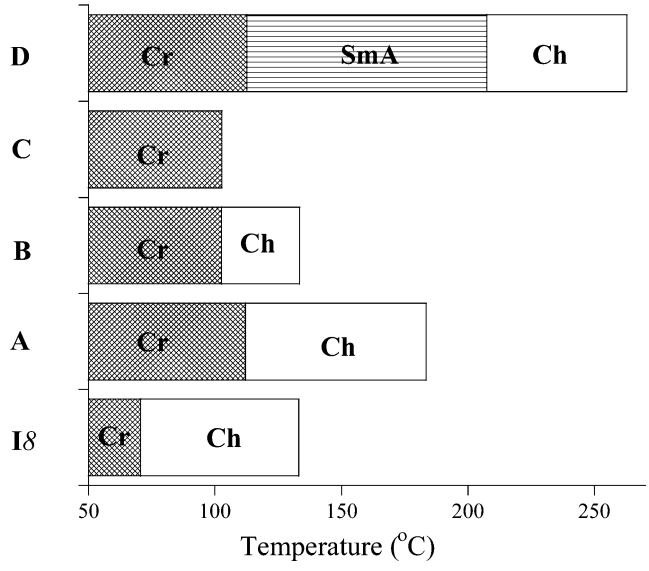


Figure 2. Comparison of mesomorphic properties of compounds **I8**, **A**, **B**, **C** and **D**.

Table 2. Transition temperatures of compounds **II*n*** (Cr=crystal; BP=blue phase; Ch=cholesteric phase; I=isotropic liquid; Recr=recrystallization).

Compound	*n*	Transition temperatures /°C
II4	4	Cr 65.9 Ch 143.8 I 143.2 Ch 56.8 Recr
II5	5	Cr 66.1 Ch 134.2 BP 134.8 I 133.5 BP 133.0 Ch 56.1 Recr
II6	6	Cr 66.7 Ch 135.2 BP 135.7 I 134.4 BP 134.0 Ch 59.6 Recr
II7	7	Cr 63.8 Ch 128.5 BP 129.2 I 127.6 BP 127.1 Ch 57.8 Recr
II9	9	Cr 79.1 Ch 126.9 BP 127.2 I 126.0 BP 125.4 Ch 47.9 Recr

seems that the polarity of the liquid crystalline cores strongly affects the liquid crystalline phases. Because alkoxy chains are electron doners and carboxy group is electron acceptor, the previous compounds exhibit higher polarity than compounds **I*n*** and **II*n***.

In summary, some chiral LCs with 1,4-tetrafluorophenylene units have been synthesized. Nearly all of them exhibit an enantiotropic cholesteric phase. Lateral tetrafluoro substitution strongly decreases the clearing points of the LCs. Moreover, it was found that lateral nitro substitution also decreases the clearing points. However, the introduction of 1,4-phenylene group increases the clearing point and enhances the formation of a smectic phase. With the introduction carboxy groups between the chiral alkoxy and 1,4-phenylene groups, the polarity of the molecules is decreased and the clearing points are decreased and blue phases are formed.

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