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Synthesis and mesomorphic properties of tolane-based liquid crystals with a fluorinated polar end group

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Three series of tolane-based liquid crystalline compounds with a fluorinated polar end group have been synthesized. Their phase transition temperatures were measured by texture observation in a polarizing microscope and confirmed by DSC. The all-fluorinated trifluoromethyl and trifluoromethoxy group have a tendency to promote the smectic A phase, but the difluoromethoxy group has the tendency to promote a wide nematic phase.

1. Introduction

In the last twenty years the LCD market has shown a significant growth starting from simple TN applications, including watches and calculators, and leading to displays with information content such as in notebook computers. In order to fulfill the requirements of high resolution and large size LCDs, advanced liquid crystal materials have been developed [1–5]. An increasing amount of research has been carried out on the synthesis of liquid crystals (LCs) to search out new potential materials for display devices. Recently, considerable attention has been paid to the synthesis of tolane-based LCs, which possess both low viscosity and high birefringence [6–14]. From another point of view, LCs with a polar end group usually exhibit large dielectric anisotropy parallel to the molecular axis, which can reduce the LCD driving voltage. As a result, fluorinated polar end groups such as trifluoromethyl, trifluoromethoxy, difluoromethoxy, etc., have been widely used in the design of liquid crystalline compounds for LCD displays [15–18]. Some new tolane-based LCs with a fluorinated polar end unit have therefore been designed for the purpose of studying their chemical structure–mesomorphic properties relationship.

2. Experimental

2.1. *Characterization*

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 solids or films of liquids. ^{1}H NMR spectra with tetramethylsilane (TMS) as internal standard, and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard, were recorded on a Bruker300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope using electrical ionization. The phase behaviour of the target compounds was measured visually by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Metter 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 $5^\circ\mathrm{C\,min^{-1}}$). 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 in the literature [19–21].

2.2. *Synthesis*

The synthesis of target compounds is outlined in scheme 1. 4-Alkoxyphenylacetylene and 4-difluoromethoxybenzaldehyde (**6**) were prepared by reported methods [22, 23]. The oxidation of **6** by $KMnO_4$ afforded the 4-difluoromethoxybenzoic acid (**7**). Esterification of the corresponding benzoic acids (**1**, **3** and **7**) and 4-iodophenol in the presence of DCC and DMAP in dry CH_2Cl_2 afforded the compounds **2**, **4** and **8**. The target compounds **A*n***, **B*n*** and **C*n*** could be obtained by the coupling reaction of compounds **2**, **4**

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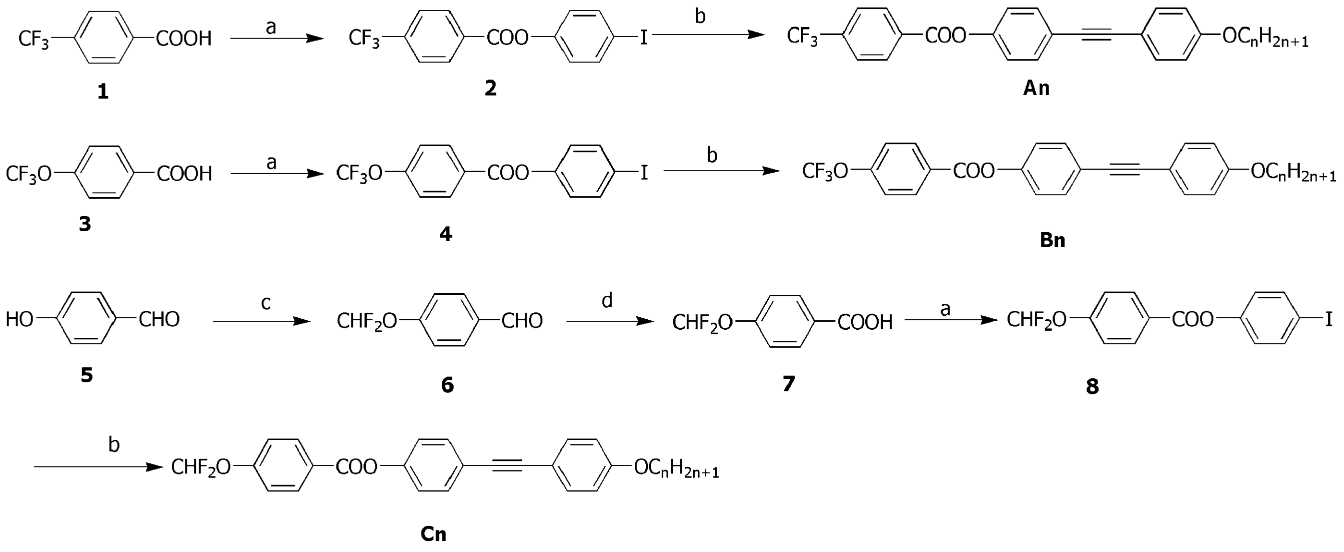

Reagents and conditions: a) 4-iodophenol, DCC, DMAP, CH_2Cl_2; b) 4-alkoxyphenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N; c) NaOH, 1,4-dioxane, CHF_2Cl; d). $KMnO_4$, H_2O.

Scheme 1. Synthetic route for the target compounds.

and **8**, respectively, with 4-alkoxyphenylacetylene using $Pd(PPh_3)_2Cl_2$ as catalyst.

2.2.1. 4-Iodophenyl 4-trifluoromethylbenzoate (2). 4-Trifluoromethylbenzoic acid (3 g, 0.0158 mol), 4-iodophenol (4.1 g, 0.0186 mol), DCC (4.0 g, 0.0194 mol), catalytic DMAP (10 mg) and dry CH_2Cl_2 (30 ml) were stirred under N_2 atmosphere at room temperature for 24 h. The mixture was filtered and the residue washed with CH_2Cl_2. The collected filtrates were evaporated in a rotary evaporator. The residue was purified by flash chromatography and recrystallized from hexane to give a white solid (4.8 g, yield 78%). δ_H ($CDCl_3$): 6.9–8.3 (m, 4H) ppm. δ_F ($CDCl_3$) −13.3 ppm. *m*/*z*(%): 392 (M^+, 15.92), 173 ($CF_3C_6H_4CO^+$, 100.0).

2.2.2. 4-Iodophenyl 4-trifluoromethoxybenzoate (4). Compound **4** was prepared by a similar procedure to compound **2**; yield 73%. δ_H ($CDCl_3$): 6.92–7.02(m, 2H), 7.24–7.38(m, 2H), 7.59–7.68(m, 2H), 8.19–8.28(m, 2H) ppm. δ_F ($CDCl_3$): -19.0(s, 3F) ppm. MS (*m*/*z*): 408(M^+, 5.80), 189($CF_3OC_6H_4CO^+$, 100.0).

2.2.3. 4-Difluoromethoxybenzoic acid (7). 4-Difluorobenzaldehyde (22.5 g, 0.13 mol) and 300 ml of water were placed in a flask heated to 70–80°C in an oil bath, with stirring, a solution of $KMnO_4$ in 300 ml of water was added to the mixture over a period of 45 min. Sufficient 10% potassium hydroxide solution was then added to make the solution alkaline. The mixture was filtered hot, and the solid washed with hot water. The combined filtrate and washings were cooled and acidified with hydrochloric acid until no further precipitate was formed. The resulting solid was filtered, washed with cold water, and dried; yield 18.4 g (75%). δ_H (CD_3COCD_3): 6.64(t, 1H, $J_{H\text{-}F}=$ 73 Hz, C*H*F_2O), 6.79(m, 2H), 7.61(m, 2H) ppm; δ_F(CD_3COCD_3): 6.6(d, 2F, $J_{H\text{-}F}=73$Hz) ppm. MS (*m*/*z*): 188(M^+, 98.93), 121 (100.0).

2.2.4. 4-Iodophenyl 4-difluoromethoxybenzoate (8). Compound **8** was prepared by a similar procedure to compound **2**; yield 81%. δ_H ($CDCl_3$): 6.65(t, 1H, $J_{H\text{-}F}=73$ Hz, C*H*F_2O), 6.96–7.06(m, 2H), 7.19–7.29(m, 2H), 7.71–7.81 (m, 2H), 8.19–8.28(m, 2H) ppm; δ_F($CDCl_3$): 6.3(d, 2F, $J_{H\text{-}F}=73$Hz) ppm. MS (*m*/*z*): 390(M^+, 4.29), 171($CHF_2OC_6H_4CO^+$, 100.0).

2.2.5. 4-[(4-*n*-Butoxyphenyl)ethynyl]phenyl 4-trifluoromethybenzoate (A4). All the final fifteen compounds were prepared using the same methods and therefore the general experimental procedures are illustrated using 4-[(4-*n*-butoxyphenyl)ethynyl]phenyl 4-trifluoromethybenzoate (**A4**) as an example. Representation characterization data are given for compounds **A**, **B** and **C**. A mixture of compound **2**(200 mg, 0.51 mmol), 4-*n*-butoxyphenylacetylene (116 mg, 0.612 mol), bis(triphenylphosphine)palladium dichloride (10 mg), copper(I) iodide (15 mg) and 10 ml of anhydrous triethylamine was stirred at 50°C for 24 h. The precipitate formed was filtered and washed with ether, and the filtrate was washed with water and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using hexane/dichloromethane (3/1) as eluant, to give a pale yellow crystals which were recrystallized from hexane to yield white flaky crystals of compound **A4**; yield 164.7 mg (73%), m.p. 142.0°C. δ_H (CDCl$_3$): 0.99(t, 3H, J=7.49 Hz, CH_3), 1.46–1.57(m, 2H), 1.75–1.80(m, 2H), 3.98(t, 2H, J=6.51 Hz, OCH_2), 6.86–6.89(m, 2H), 7.20–7.23(m, 2H), 7.45–7.48(m, 2H), 7.57–7.60(m, 2H), 7.77–7.80(m, 2H), 8.30–8.33(m, 2H) ppm; δ_F (CDCl$_3$): −14.3(s, 3F) ppm. MS *m*/*z* (rel. int.): 438(M$^+$, 33.77), 173(CF$_3$C$_6$H$_4$CO$^+$, 100.0). Anal. for C$_{26}$H$_{21}$F$_3$O$_3$: calcd C 71.23, H 4.83, F 13.00%; found C 71.49, H 4.97, F 12.80%. υ_{max} (KBr): 2961, 2930, 2871, 2219, 1728, 1605, 1513, 1412, 1255, 1214, 1169, 1021, 829.

2.2.6. 4-[(4-*n*-Butoxyphenyl)ethynyl]phenyl 4-trifluoromethoxybenzoate (B4). ^{1}H NMR δ_H (300 Mhz, CDCl$_3$, TMS): 0.98(t, 3H, J=7.33 Hz, CH_3), 1.46–1.56(m, 2H), 1.73–1.83(m, 2H), 3.98(t, 2H, J=6.52 Hz, OCH_2), 6.86–6.90(m, 2H), 7.17–7.22(m, 2H), 7.33–7.36(m, 2H), 7.44–7.48(m, 2H), 7.55–7.59(m, 2H), 8.23–8.28(m, 2H) ppm; ^{19}F NMR δ_F (60MHz, CDCl$_3$, TFA): −20.3(s, 3F) ppm. MS *m*/*z* (rel. int.): 454(M$^+$, 29.10), 189(100.0). Anal. for C$_{26}$H$_{21}$F$_3$O$_4$: calcd C 68.72, H 4.66, F 12.54%; found C 68.90, H 4.73, F 12.28%. υ_{max} (KBr): 2961, 2931, 2873, 2220, 1727, 1605, 1514, 1411, 1319, 1254, 1167, 1022, 829.

2.2.7. 4-[(4-*n*-Butoxyphenyl)ethynyl]phenyl 4-difluoromethoxybenzoate (C4). ^{1}H NMR δ_H (300 MHz, CDCl$_3$, TMS): 1.00(t, 3H, J=7.16 Hz, CH_3), 1.47–1.59(m, 2H), 1.75–1.84(m, 2H), 3.99(t, 2H, J=6.34 Hz, OCH_2), 6.64(t, 1H, $J_{H\text{-}F}$=73.1 Hz), 6.87–6.90 (m, 2H), 7.20–7.27(m, 4H), 7.46–7.49(m, 2H), 7.57–7.59(m, 2H), 8.22–8.25(m, 2H) ppm; ^{19}F NMR δ_F (60 MHz, CDCl$_3$, TFA): 3.5(d, 2F, $J_{H\text{-}F}$=73.1 Hz) ppm. MS *m*/*z* (rel. int.): 436(M$^+$, 53.55), 171(100.0). Anal. for C$_{26}$H$_{22}$F$_2$O$_4$: calcd C 71.55, H 5.08, F 8.71%; found C 71.53, H 4.75, F 8.75%. υ_{max} (KBr): 2955, 1727, 1605, 1513, 1474, 1287, 1250, 1216, 1165, 1052, 828.

3. Results and discussion

The transition temperatures of series **A*n***, **B*n*** and **C*n*** were measured by DSC, and phase identification was made by comparing the observed textures with those reported in the literature. The results are summarized in table 1. The transition temperatures of series **A*n***, **B*n*** and **C*n*** are plotted against the number of carbon atoms in the alkoxy chain, *n*, in figures 1, 2 and 3, respectively.

As can be seen from figures 1, 2 and 3, for series **A*n***, with a trifluoromethyl group as the end group, a very wide smectic A phase is observed; a narrow nematic phase is seen when the alkoxy chain is short (under 6 carbon atoms), and a higher ordered smectic B phase emerges when the alkoxy chain becomes longer. The melting points and clearing temperatures are decrease with the longer alkoxy chains. The series **B*n***, with a trifluoromethoxy group as the end group, show similar mesophases to series **A*n***, with the difference that the nematic phase of series **B*n*** is wider than for series **A*n***, and the smectic B phase emerges at a shorter alkoxy chain length, The series **C*n***, with a difluoromethoxy group as the end group, shows a very simple mesophase

Table 1. Phase transition temperatures of target compounds. Cr=crystal; SmA=smectic A phase; SmB=smectic B phase; SmX=unknown smectic phase; N=nematic phase; I=isotropic; Recr=recrystallisation.

Compound	*n*	Transition temperature/°C
A4	4	Cr 142.0 SmA 204.8 N 218.8 I 217.0 N 202.6 SmA 131.1 Recr
A5	5	Cr 126.6 SmA 204.2 N 209.3 I 204.2 N 209.3 SmA 121.6 SmB 112.5 Recr
A6	6	Cr 123.0 SmA 205.6 N 206.7 I 205.2 N 203.7 SmA 121.3 SmB 113.5 Recr
A7	7	Cr 117.9 SmB 122.9 SmA 202.8 I 201.0 SmA 121.6 SmB 102.8 Recr
A8	8	Cr 115.3 SmB 123.9 SmA 201.5 I 200.2 SmA 122.7 SmB 99.0 Recr
B4	4	Cr 126.7 SmA 195.9 N 233.4 I 231.9 N 193.9 SmA 118.3 SmB 114.9 Recr
B5	5	Cr 109.5 SmB 116.7 SmA 199.0 N 222.5 I 220.9 N 197.1 SmA 115.1 SmB 106.8 SmX 89.2 Recr
B6	6	Cr 107.4 SmB 117.6 SmA 201.6 N 217.7 I 216.0 N 200.0 SmA 115.9 SmB 105.5 SmX 89.2 Recr
B7	7	Cr 107.3 SmB 118.0 SmA 201.2 N 210.3 I 208.8 N 199.6 SmA 116.5 SmB 101.8 SmX 86.0 Recr
B8	8	Cr 105.3 SmB 119.7 SmA 201.1 N 206.2 I 204.7 N 199.3 SmA 118.1 SmB 98.9 SmX 83.5 Recr
C4	4	Cr 122.5 N 242.9 I 241.6 N 103.2 Recr
C5	5	Cr 114.5 N 230.4 I 228.2 N 90.8 Recr
C6	6	Cr 109.9 N 224.8 I 223.1 N 93.4 Recr
C7	7	Cr 109.1 N 216.1 I 212.8 N 92.5 Recr
C8	8	Cr 107.6 N 210.9 I 209.2 N 98.2 SmA 87.0 Recr

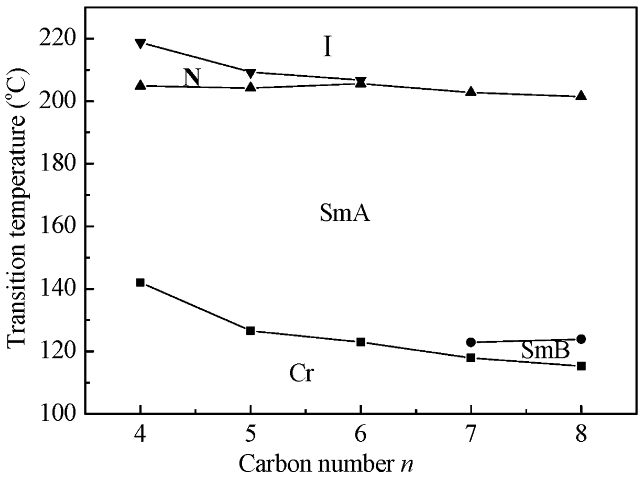

Figure 1. Transition behaviour of Series **A*n***: dependence of transition temperature on the carbon number of the alkoxy chain.

sequence, with only a very wide nematic phase (over 110°C). All three series show very good thermal stability, and the melting points and clearing temperatures are relatively high.

All the three end groups have a relatively high polarity: CF_3 2.56 D; OCF_3 2.36 D; $OCHF_2$: 2.46 D [24]. They also can be regarded as very short fluorinated aliphatic chains, so their effects on mesomorphic properties are similar to long fluorinated chains. Thus all-fluorinated groups such as trifluoromethyl and trifluoromethoxy facilitate the form ation of smectic phases; but the terminal hydrogen atom in the difluoromethoxy group increases the attracting forces at the end of the molecule, enhancing the tendency to form a nematic phase. Although the hydrogen atom in the difluoromethy group is acidic, its stability in LCD applications has recently been demonstrated and the voltage-holding rate of mixtures contained this kind of LC material is extremely high [24]. So the series **C*n*** with both broad a nematic phase range and the excellent properties of the difluoromethoxy group should provide good candidate materials for nematic-type LCD displays.

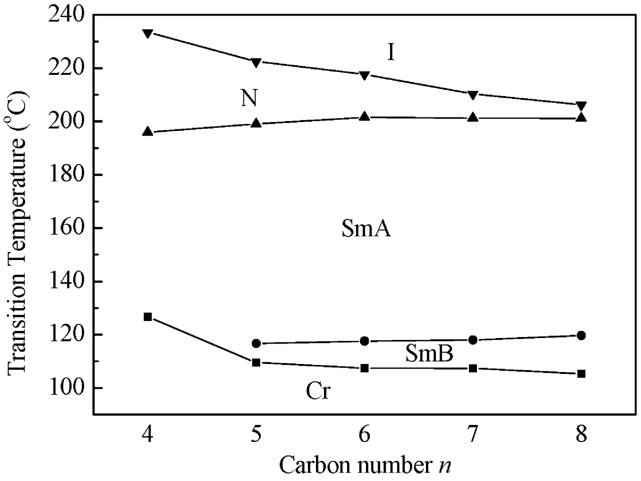

Figure 2. Transition behaviour of Series **B*n***: dependence of transition temperature on the carbon number of the alkoxy chain.

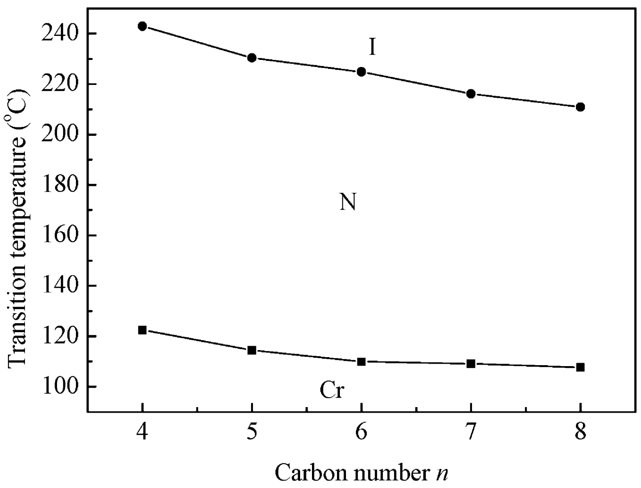

Figure 3. Transition behaviour of Series **C*n***: dependence of transition temperature on the carbon number of the alkoxy chain.

In conclusion, this investigation reveals that polar fluorinated end groups vary remarkably in their mesomorphic properties. The all-fluorinated CF_3 and OCF_3 have the tendency to form smectic A phases, but the difluoromethoxy group has the tendency to form the nematic phase. In relation to the polarity and voltage holding rate of the difluoromethoxy-containing compounds, the series **C*n*** compounds have good potential application for LCD displays.

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