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Synthesis and mesomorphic properties of 4-[(4-*n*-polyfluoroalkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl fluoro-substituted benzoates

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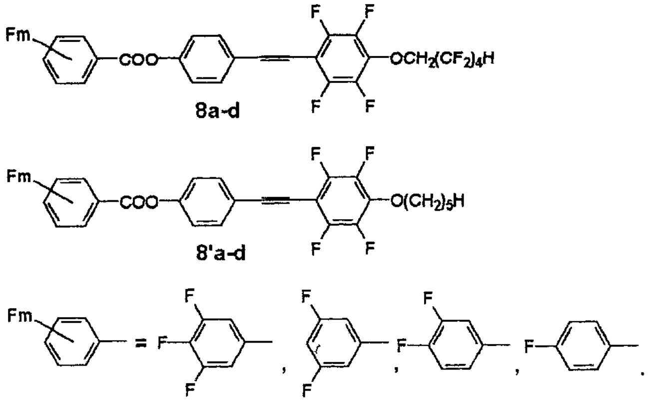
A series of 4-[(4-*n*-polyfluoroalkoxy-2,3,5,6-tetrafluorophenyl)ethynyl]phenyl fluoro-substituted benzoate liquid crystals have been synthesized. Their phase transition temperatures have been measured by optical polarizing microscopy and confirmed by DSC. The results show that a highly fluorinated terminal chain impairs mesomorphic properties.

1. Introduction

Fluorinated liquid crystals (LCs) have been closely studied in the past decade due to their unique properties, such as low viscosity, low conductivity and high chemical and thermal stability. The 2,3,5,6-tetrafluorotolanes, as reported by our group, possess high birefringence and many other advantages [1–5], and are valuable as components of mixtures for electro-optical applications such as STN and TFT LCDs. As we know, LCs containing polyfluoroalkyl terminal chains are advantageous to the formation of tilted smectic phase [6, 7] and are valuable as potentially important components of mixtures for ferroelectric liquid crystals displays (FLCDs). In order to meet the higher quality requirements for materials and observe the relationship between structures and properties, the synthesis of mesogens containing a moiety that combines the two above-mentioned units was desired. This paper now reports results on novel liquid crystalline compounds with the 4-polyfluoroalkoxy-2,3,5,6-tetrafluorophenylethynyl unit introduced into the core, as shown in scheme 1. Relationships between the molecular structure and mesomorphic properties are discussed.



Scheme 1.

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 Bruker 300 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 transition temperatures of the target compounds were measured visually 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. Phase identification was made by comparing the observed textures and those previously reported [8, 9].

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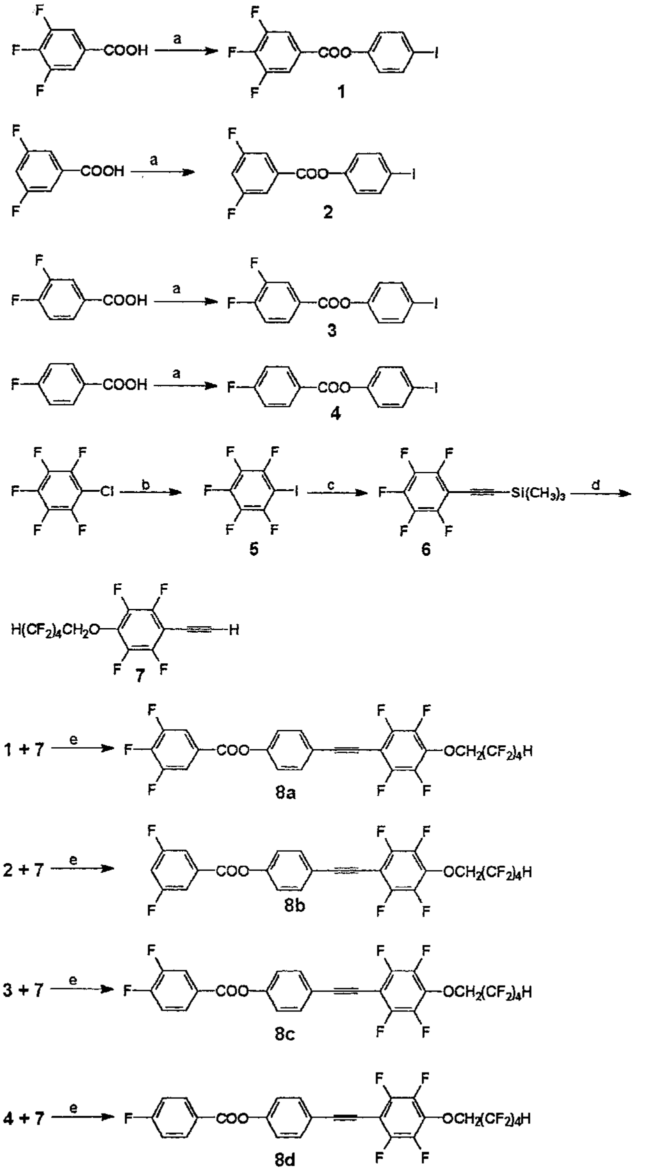
2.2. *Synthesis*

The synthesis of the target compounds is outlined in scheme 2. The preparation of compound **6** was reported previously [10]. The fluoro-substituted benzoic acid can be easily obtained according to a reported procedure [11].

Pentafluorochlorobenzene was reacted with magnesium filings in anhydrous tetrahydrofuran (THF) solution below −10°C, iodine was then added to the resulting Grignard reagent to give pentafluoroiodobenzene **5**. Compound **5** was then coupled with trimethylsilylacetylene using bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalyst in anhydrous triethylamine solution; the product was trimethylsilylethynyl-2,3,4,5,6-pentafluorobenzene **6**. The fluorosubstituent on the *para*-position of compound **2** was then substituted by the 2,2,3,3,4,4,5,5-octafluoropentoxy group in a basic medium, leaving the protected trimethylsilyl group. Thus 4-(2,2,3,3,4,4,5,5-octafluoropentoxy)-2,3,5,6-tetrafluorophenylacetylene **7** was obtained. Target compounds (**8a–d**) were prepared by the cross-coupling reaction between **7** and appropriate *p*-iodophenyl fluoro-substituted benzoates (**1–4**) using bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalyst in anhydrous triethylamine solution.



Reagents and Conditions: (a) p-iodophenol, DCC, cat. DMAP, CH_2Cl_2, r. t.; (b) Mg, then I_2, ethyl ether; (c) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N; (d) $H(CF_2)_4CH_2OH$, K_2CO_3, DMF; (e) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N.

Scheme 2.

2.2.1. *4-[(2′,2′,3′,3′,4′,4′,5′,5′-Octafluoropentoxy)-2,3,5,6-tetrafluorophenyl]acetylene (7)*

Trimethylsilylethynyl-2,3,4,5,6-pentafluorobenzene **6** (4.00 g, 15.16 mmol), potassium carbonate (2.54 g, 18.40 mmol), 2,2,3,3,4,4,5,5-octafluoropentanol (5.08 g, 21.9 mmol) and anhydrous *N,N*-dimethylformamide (50 ml) were mixed in a 100 ml flask and stirred at room temperature. ^{19}F NMR was used to monitor the reaction solution until the reagent had disappeared. Diethyl ether (50 ml) and water (20 ml) were then added to the flask and the mixture was extracted with diethyl ether. The ether extracts were washed neutral with brine and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as eluent to give **7** as a colourless liquid; yield 1.92 g (63%). ^1H NMR ($CDCl_3$/TMS, 90 MHz) δH (ppm): 3.46 (s, 1H), 4.62 (t, 2H, $J = 13$ Hz), 5.95 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 6$ Hz). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δF (ppm): 44.4 (t, 2F, $J = 13$ Hz), 48.7 (m, 2F), 53.6 (m, 2F), 59.5–61.7 (m, 4F), 79.5 (d, 2F, $J = 24$ Hz).

2.2.2. *4-[(2′,2′,3′,3′,4′,4′,5′,5′-Octafluoropentoxy-2,3,5,6-phenyl)ethynyl]phenyl 3,4,5-trifluorobenzoate (**8a**)*

In a typical procedure, **7** (250 mg, 0.496 mmol), *p*-iodophenyl 3,4,5-trifluorobenzoate (**1**, 151 mg, 0.40 mmol), bis(triphenylphosphine)palladium dichloride (30 mg), copper(I) iodide (50 mg), triphenylphosphine (80 mg) and anhydrous triethylamine (15 ml) were add to a 25 ml flask. The resulting mixture was stirred at 60°C for 48 h under nitrogen. After the reaction was completed, the precipitate formed was filtered off and washed with water, then dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20:1) as the eluent. This gave pale yellow crystals which were recrystallized from methanol to yield white flaky crystals of **8a**; yield 178 mg (68%). MS (*m/z*): 654 (M^+), 159 ($C_6H_2F_3CO^+$, 100.00). Anal. for $C_{26}H_9F_{15}O_3$: calc. C 47.73, H 1.38, F 43.56; found C 47.66, H 1.50, F 43.80%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 4.70 (t, 2H, $J = 13$ Hz), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5$ Hz), 7.24–7.27 (m, 2H), 7.64–7.67 (m, 2H), 7.84–7.88 (m, 2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 43.4 (m, 2F), 47.7 (m, 2F), 52.5 (m, 2F), 54.7 (m, 2F), 58.5–60.8 (m, 4F), 73.7 (m, 1F), 80.6 (m, 2F). IR (KBr, ν_{max}, cm^{-1}): 2224, 1743, 1605, 1498, 1445, 1256, 1176, 1206, 1049, 817, 756.

2.2.3. *4-[(2′,2′,3′,3′,4′,4′,5′,5′-Octafluoropentoxy-2,3,5,6-phenyl)ethynyl]phenyl 3,5-difluoro-benzoate* (**8b**)

MS (*m/z*): 637 ($M^+ + 1$, 17.26), 141 ($C_6H_3F_2CO^+$, 100.00), 113 ($C_6H_3F_2^+$, 17.56). Anal. for $C_{26}H_{10}F_{14}O_3$: calc. C 49.08, H 1.57, F 41.80; found C 49.26, H 1.86, F 42.33%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 4.70 (t, 2H, $J = 13$ Hz), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5$ Hz), 7.09–7.15 (m, 1H), 7.26–7.29 (m, 2H), 7.64–7.74 (m, 4H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 32.3 (m, 2F), 45.3 (m, 2F), 49.6 (m, 2F), 54.8 (m, 2F), 61.0–62.7 (m, 4F), 81.3 (m, 2F). IR (KBr, ν_{max}, cm^{-1}): 2224, 1736, 1599, 1493, 1444, 1285, 1220, 1126, 1083, 866, 840.

2.2.4. *4-[(2′,2′,3′,3′,4′,4′,5′,5′-Octafluoropentoxy-2,3,5,6-phenyl)ethynyl]phenyl 3,4-difluoro-benzoate* (**8c**)

MS (*m/z*): 637 ($M^+ + 1$, 9.12), 141 (100.00), 113 (18.87). Anal. for $C_{26}H_{10}F_{14}O_3$: calc. C 49.08, H 1.57, F 41.80; found C 49.32, H 1.65, F 41.99%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 4.70 (t, 2H, $J = 13$ Hz), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5$ Hz), 7.25–7.37 (m, 3H), 7.48–7.67 (m, 2H), 8.00–8.06 (m, 2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 43.1 (m, 2F), 48.5 (m, 2F), 50.9 (m, 1F), 52.3 (m, 2F), 58.0–60.3 (m, 5F), 79.4 (m, 2F). IR (KBr, ν_{max}, cm^{-1}): 2224, 1743, 1619, 1494, 1444, 1297, 1270, 1132, 1066, 895, 809.

2.2.5. *4-[(2′,2′,3′,3′,4′,4′,5′,5′-Octafluoropentoxy-2,3,5,6-phenyl)ethynyl]phenyl 4-fluoro-benzoate* (**8d**)

MS (*m/z*): 619 ($M^+ + 1$, 4.48), 123 (100.00), 95 (20.32). Anal. for $C_{26}H_{11}F_{13}O_3$: calc. C 50.51, H 1.78, F 39.95; found C 50.51, H 1.65, F 40.32%. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ_H (ppm): 4.70 (t, 2H, $J = 13$ Hz), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5$ Hz), 7.18–7.28 (m, 4H), 7.63–7.68 (m, 2H), 8.21–8.26 (m, 2H). ^{19}F NMR ($CDCl_3$/TFA, 56.4 MHz) δ_F (ppm): 28.5 (m, 2F), 45.7 (m, 2F), 50.0 (m, 1F), 54.8 (m, 2F), 61.0–63.0 (m, 4F), 81.7 (m, 2F). IR (KBr, ν_{max}, cm^{-1}): 2224, 1739, 1606, 1492, 1445, 1265, 1198, 1156, 1070, 853.

3. Results and discussion

The phase transition behaviours of the target compounds are summarized in the table. The mesomorphic properties of these compounds are decided by the number and position of the fluoro substituents; the sample with 3,4,5-trifluoro only shows a very narrow enantiotropic nematic phase, while sample with 3,5-difluoro only exhibits a very narrow enantiotropic smectic A phase. For samples with 3,4-difluoro and 4-fluoro, both enantiotropic nematic and smectic A phases were observed. It is worth noting that in these cases, a *para*-fluoro substituent increases melting points (**8a** > **8b**), and one *meta*-fluorosubstituent decrease melting points (**8d** > **8c**), but the second *meta*-fluorosubstituent increases melting points (**8a** > **8d**). The melting points order is thus 3,4,5-trifluoro > 4-fluoro > 3,5-difluoro > 3,4-difluoro. On the other hand, a *para*-fluoro substituent increases clearing points and a *meta*-fluorosubstituent decreases clearing points; the clearing points order is thus 4-fluoro > 3,4-difluoro > 3,4,5-trifluoro > 3,5-difluoro. These phenomena are considered to result from the *para*-fluoro-substituent increasing the length-width ratio, while the *meta*-fluorosubstituent decreases it. Also, a *meta*-fluoro substituent is disadvantageous to the formation of the smectic A phase in systems containing highly fluoro-substituted alkyl terminal chains (**8d** > **8c** > **8a**). Thus the laterally fluoro substituent suppresses the smectic phase.

As mentioned above, our target was to synthesize mesogens with a 4-polyfluoroalkoxy-2,3,5,6-tetrafluoro-tolane unit in the core and compare their mesomorphic properties with those of homologues containing the 4-alkoxy-2,3,5,6-tetrafluorotolane unit (**8′a–d**, scheme 1) [12]. The result is shown in the figure, from which the difference between the highly fluorinated alkyl terminal chains and soft hydrocarbon terminal chains is shown. These eight compounds are divided into four groups **a**, **b**, **c** and **d**; for example, **8a** and **8′a** in group **a**. We can see that highly fluorinated alkyl terminal chains increase the melting points in all groups and decrease the clearing points in groups **a**, **c** and **d**, thus greatly impairing mesomorphic properties in all groups. It is well known that

Table. Phase transition temperature of target compounds. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic liquid, Recr = recrystallization.

Compound	Transition temperature/°C
8a	Cr 103.3 N 103.7 I 101.6 N 62.1 Recr
8b	Cr 97.6 SmA 98.2 I 97.6 SmA 64.6 Recr
8c	Cr 94.4 SmA 106.6 N 129.4 I 126.9 N 103.0 SmA 51.1 Recr
8d	Cr 102.0 SmA 140.2 N 156.9 I 155.4 N 138.4 SmA 72.1 Recr

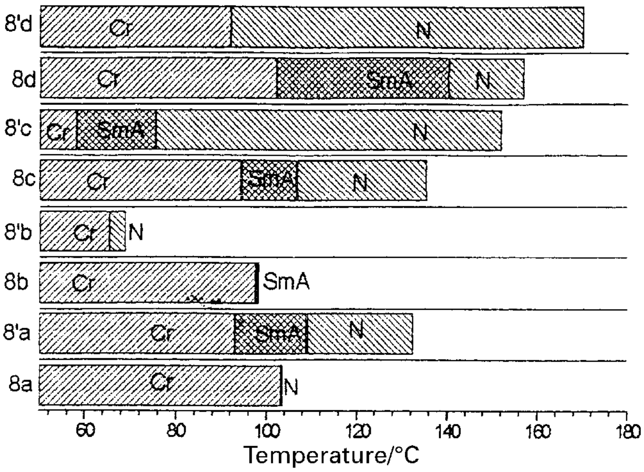


Figure. Comparison of mesomorphic properties of compounds **8a-d** and **8′a-d**.

highly fluorinated alkyl terminal chains are advantageous to the formation of smectic phase; this conclusion can be observed in groups **b**, **c** and **d**, but in group **a** only a very narrow nematic phase is shown in **8a**.

In conclusion, 4-polyfluoroalkoxy-2,3,5,6-tetrafluorotolanes exhibit poorer mesomorphic properties than corresponding 4-alkoxy-2,3,5,6-tetrafluorotolanes. It is considered that highly fluorinated alkyl terminal chains are advantageous to the formation of smectic phases, but not the nematic phase; however, 2,3,5,6-tetrafluorophenyl is advantageous to the formation of the nematic phase and it can depress smectic phases. So the combination of these two contradictary characteristics impairs all mesophases.

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